

or reactive silanes. After evaporation of solvent and setting or cure of the primed surface, the rubber compounds are applied and cured under pressure. Self-bonding silicone rubber stocks require no primer (352,388).

Silicone rubber is compounded in dough mixers, Banbury mixers, two-roll rubber mills, various types of change-can mixers, and continuous compounders. Large vertical Banbury mixer systems are used for high volume semicontinuous production of dry (but not overly tacky) compounds; tackiness can create problems in unloading (342). The basic process requirements are similar in all cases: addition of gums, fillers, process aids, pigments, and catalysts in the prescribed order; breakdown of agglomerates in the fillers; uniform dispersion of filler in the gum; and control of temperature and, in some cases, pressure for retention or removal of volatile ingredients and prevention of premature cure.

The earliest compounding mixer was the two-roll mill, which remains the most flexible device for custom pigmentation or catalysis of small lots. A mill for one-person operation is limited to a roll diameter of up to ca 0.5 m and a roll width of up to ca 2 m; such a mill can handle batches of up to 70 kg. The rolls typically operate at face speeds of ca 30 m/min with a differential speed ratio between rolls of 1.1–1.4. Auxiliary features include pneumatically operated end guides and scraper blades, knee- and arm-actuated safety cutouts with instantaneous braking action, temperature control by internal water cooling, and an exhaust hood to remove fine-particle dusts.

Heat-cured rubber formulations vary widely; a typical compound might have the composition given in Table 18. In processing, the polymer is placed on the mill rolls, and the reinforcing filler is added in increments with varying mill speed and clearance to obtain uniform dispersion of the filler in the gum. Process aids promote softening or plasticizing and are used with reinforcing silica fillers to prevent hardening (353,408,409). The rubber is periodically peeled from one edge of the rolls and cross-blended to the opposite side to ensure batch uniformity. After the reinforcing filler is completely dispersed, the other ingredients are added in a prescribed order, with mixing after each addition. The completed compound issues from the mill in strips and is packaged or stored for final extrusion (388,406).

**Table 18. Formulation of Heat-cured Silicone Rubber**

Component	Parts by weight
silicone polymer	100
reinforcing filler	30
nonreinforcing filler	70
process aids or other additives	10
pigment	1

Silicone rubber compounds are frequently shipped without catalyst. The proper peroxide, usually dispersed in paste form in a silicone polymer, is added by the customer just before use. The two-roll mills are widely used for catalyst addition because they provide good temperature control. Heating the compound above 50°C, especially when using 2,4-dichlorobenzoyl peroxide as curing catalyst, can initiate cross-linking and affect processibility.

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Dough mixers with tangential or overlapping blade design are widely used for compounding large batches of viscous heat-curing compounds. These mixers are typically of steel or stainless steel construction, with multiple speed drives and high power input, equivalent to as much as 0.6 J/kg (2.5 cal/kg) of charge. The batch size ranges up to a few thousand kilograms for dough mixers of ca 2-m<sup>3</sup> capacity. The equipment is jacketed for heating and cooling and equipped with a pressure- and vacuum-tight lid and a hood for exhausting dust and fumes. Because of the high shearing forces generated and the high volume resistivity of silicone polymer, strong localized electrical charges are built up during the compounding operation, resulting in static discharge. The dough-mixer body is therefore purged with an inert gas to sweep out volatile materials and prevent formation of a combustible mixture.

The compounding sequence for dough mixers is similar to that for rubber mills: the gum is placed in the mixer, and the fillers are added incrementally, either manually from bags or from batch hoppers that have been loaded by pneumatic transfer. The mixing cycle may include operation at elevated temperatures to remove volatiles or improve the effectiveness of the blending operation. Mixing with the rubber mill is more effective than with a dough mixer, but the compounding cycle is several times as long. However, there is a significant saving in labor because of larger batches and reduced manual handling; product uniformity is higher. After the time requirements for the various mixing stages have been determined, the sequence of operations may be automatically programmed. In other respects, such as reproducibility of compound properties and power consumption, the two compounding methods are about equally effective (415).

For highly loaded, tough compounds, Banbury mixers or dough mixers with dispersion blades achieve extremely high shear and good filler dispersion. Continuous-compounding equipment is most effective for producing reinforced gums or partial formulations containing primarily the polymer and the reinforcing filler, which is the most difficult to disperse. The reinforced gums can be used as the base for the finished products to provide a wide range of physical properties and processing characteristics.

Finishing operations usually involve extrusion of heat-curing compounds through a fine screen (100–270  $\mu$ m or 50–150 mesh) to remove filler agglomerates or foreign particles. This requires a piston- or screw-type extruder capable of generating pressures of 10–30 MPa (1450–4350 psi). This operation must be carried out before adding the catalyst since the temperatures and pressures generated in the extruder may cause scorching or premature cure. Slabs or sheets of finished rubber compounds are packed in boxes or as continuous strips on reels to permit continuous feeding into the customer's extrusion equipment.

After being catalyzed the heat-curing rubber is extruded, molded, or otherwise shaped. The shaped form must be capable of undergoing a fairly rapid cure to the point where it is not further deformed by handling and can be removed from the mold or, if extruded, wound on a reel for final cure. Molding compounds catalyzed with benzoyl peroxide require an initial cure in the mold of about 15 min at 150°C. During this period the physical strength is not fully developed, and for most applications a postcure in an oven is desirable. Recently, however, compounds that develop strength more rapidly have become available and for

many applications may require only a mold or press cure. For standard compounds a postcure of several hours at 200–250°C may serve, depending on the final properties desired and the temperature range to be encountered. In general, the higher the postcure temperature, the lower the weight loss on subsequent exposure to high temperatures.

Continuous hot-air vulcanizing for extrusions and wire coatings requires a 2,4-dichlorobenzoyl peroxide curing catalyst. The extrusion or coating can be fully cured in a few seconds while passing through an electrically heated or gas-fired tunnel at 400–650°C; the product can be packaged directly in final form. For specialized applications radiation cure may be preferred, since it avoids residues with potentially deleterious effects (416).

Independent rubber fabricators usually compound from purchased reinforced gum compositions. In order to satisfy the many specialized requirements on silicone rubber fabricated items, stock grades are available containing polymer, filler, and process aids that can be combined in various proportions for particular values for hardness, tensile strength, and elongation. Additives are also available to confer heat-aging stability, flame retardancy, and oil resistance. Examples include the Silplus elastomeric system from General Electric and the Silastic compounding system elastomers from Dow Corning (342).

Silicone heat-cured rubber products are packaged in boxes of 20–50 kg; special container packages are available for quantities up to ca 500 kg (173).

**Properties.** The properties of cured silicone elastomers (Tables 13, 14, and 17) are temperature dependent; for example, Young's modulus decreases from ca 10,000 to 200 MPa ( $145 \times 10^4$  to  $2.9 \times 10^4$  psi) between –50 and 25°C and remains fairly constant to 260°C. Resistivity decreases; electric strength does not change much; the dielectric constant increases at 60 Hz current and decreases at 10<sup>6</sup> Hz current and above; and the power factor increases considerably. Tensile strength decreases from ca 6.9 MPa (1000 psi) at 0°C to 2.1 MPa (300 psi) at 300°C (352). The thermal conductivity of silicone rubber is usually ca 1.5–4 W/(m·K) and increases with increasing filler content (388).

Silicone rubber (gum) films are permeable to gases and hydrocarbons; they are ca 10–20 times as permeable as organic polymers (352,417,418). Water diffuses through lightly cross-linked gum as monomer, dimer, and trimer, with diffusion coefficients of 1.5, 3.6, and  $3.1 \times 10^{-5}$ , respectively, at 65°C (419). Silicone rubber compounds are permeable to gases (Table 19) (420). Cross-linking and fillers reduce permeability (12).

Solvents diffuse into silicone rubber and swell, soften, and weaken it. The degree of swelling depends on the solvent and has been correlated with the solubility parameters of solvent and rubber (Fig. 20). The correlation is improved if electrostatic interactions are considered (322). The solubility parameter is the square root of the energy of vaporization per cubic centimeter (421). Values for the three types of siloxane units in Figure 20 are  $(\text{CH}_3)_2\text{SiO} = 7.6$ ,  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{SiO} = 9.0$ , and  $(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{CH}_3)\text{SiO} = 9.6$ . Volume swelling can be related to cross-link density in some RTV systems (341,363).

Silicone elastomers appear completely hydrophobic to liquid water. Aqueous solutions interact with silicone rubber with varying effects. Water itself has little effect, although at higher temperatures it causes softening and weakening. If the rubber is heated with water in a sealed tube, it is converted to a sticky polymer.

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Table 19. Permeability of Silicone Elastomers<sup>a</sup>

Type	Gas	Permeability <sup>b</sup> $\mu\text{mol}\cdot\text{m}\cdot\text{s}\cdot\text{GPa}$ at 25°C
dimethylsilicone	CO <sub>2</sub>	1,090
	O <sub>2</sub>	200
	N <sub>2</sub>	93
	H <sub>2</sub> O	12,040
	C <sub>2</sub> H <sub>10</sub>	3,010
diphenylsilicone	CO <sub>2</sub>	241
	O <sub>2</sub>	42
	N <sub>2</sub>	16
fluorosilicone <sup>c</sup>	O <sub>2</sub>	38
	N <sub>2</sub>	16
nitrile silicone	CO <sub>2</sub>	224
	O <sub>2</sub>	28
	N <sub>2</sub>	11

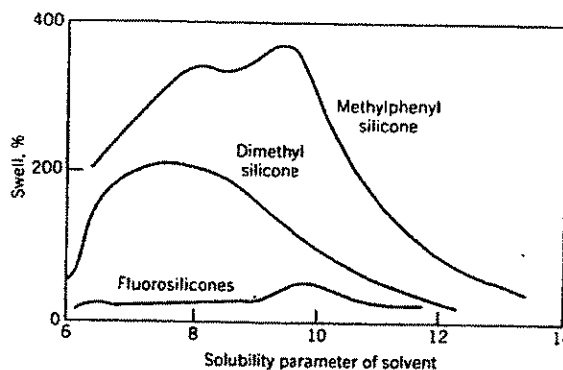
<sup>a</sup> Ref. 420.<sup>b</sup> To convert  $\mu\text{mol}/(\text{m}\cdot\text{s}\cdot\text{GPa})$  to  $\text{cc}\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{atm})$ , multiply by  $22.7 \times 10^{-9}$ .<sup>c</sup> Methyltrifluoropropyl silicone.

Fig. 20. Swelling of silicone rubber by solvents (322). Solubility parameters: for dimethylsilicone, 7.6; for methylphenylsilicone, 9.0; for methyltrifluoropropylsilicone, 9.6.

It is more strongly attacked by concentrated solutions of acids and bases (352,422). The hydrolysis that occurs is aided by catalytic species present as impurities. The activation energy for this reaction is 25 kJ/mol (6 kcal/mol), which is 71 kJ/mol (17 kcal/mol) less than that for the catalyst-free reaction (341,423).

Heat alone causes depolymerization and volatilization; the rate increases appreciably above 315°C, even in neutral compounds. Heat aging causes various changes in cured silicone rubber, which are noticed in properties at elevated temperature or after a decrease to room temperature. Heating in air at 125°C reduces elongation and increases hardness, but does not affect tensile strength (352).

Polysiloxane degradation temperatures, as measured by differential thermal analysis (dta), are given in Table 20 (341). The estimated service life of dimeth-

**Table 20. Polysiloxane Degradation Temperatures<sup>a,b</sup>**

Silicone	Oxidation temperature in dry air, °C	Rearrangement temperature <sup>c</sup> in helium, °C
ethylmethylsilicone	240	345
dimethylsilicone	290	435
methylphenylsilicone	375	410
dimethyl-methylphenyl copolymer		
74:26	300	420
44.5:55.5	350	415

<sup>a</sup> Ref. 341. Courtesy of the American Chemical Society.<sup>b</sup> By differential thermal analysis (dta); heating rate = 10°C/min.<sup>c</sup> Rearrangement temperatures could be lower than ideal because of residual trace metal impurities.

ylsilicone elastomers at elevated temperatures is shown in Table 21 (342). The data in Tables 20 and 21 are not directly comparable. The rearrangement temperatures in Table 20 are higher than those commonly encountered because the samples studied were of high purity. With typical residual ionic concentrations (from the catalyst), thermal depolymerization to cyclic compounds competes with oxidation at lower temperatures. Silicone elastomer compounds, however, contain a variety of ingredients and can be more stable toward degradation than the polymers without fillers and additives. Oxidation stability depends on the pendent organic groups. The decreasing order of stability is  $C_6H_5 > CH_3 > C_2H_5 > C_3H_7 > C_2H_3$  (vinyl) (341).

**Table 21. Estimated Service Life of Silicone Rubber<sup>a</sup>**

Temperature, °C	Years
90	40
121	10-20
150	5-10
200	2-5
250	0.25
315	0.04

<sup>a</sup> Ref. 342.

Silicone rubber can burn, but the residue is siliceous rather than carbonaceous; it has some structural integrity and is a nonconductor of electricity. The limiting oxygen index for a typical formulation is ca 20. Flame-retardant versions with limiting oxygen index values as high as 40-50 are also available (388).

Electron or gamma radiation damages cured silicone rubber. Elongation is reduced, but tensile strength is not greatly affected (424). Methylsilicone rubbers are not resistant to gamma radiation; resistance increases with degree of phenylation (425).

Silicone elastomers maintain their performance characteristics also at low temperatures. In some formulations physical properties do not deteriorate at -100°C. Substitution of phenyl for some methyl groups reduces the stiffening

temperature measured at thermal equilibrium. A dimethylsiloxane copolymer with 7.5 mol % methylphenylsiloxane exhibits an equilibrium-stiffening temperature of  $-113^{\circ}\text{C}$ , compared with  $-38^{\circ}\text{C}$  for the pure dimethylsiloxane (341,342).

Permanent deformation occurs when rubber is compressed or stretched at high temperature. This is due largely to stress relaxation caused by the rearrangement of chemical bonds; ie, the Si—O—Si bonds break and reform. The rate at which this occurs depends on the temperature, catalysts, and water. The reaction of a material to this type of change is determined by a compression set test. The degree of permanent set varies with time and temperature; values for several silicone rubbers are given in Table 17. Low compression set used to be achieved with additives, but today vinyl gums and noncatalytic components are employed (352).

Polydimethylsiloxanes have been used as model systems to study the dependence of elastic properties on structural characteristics. The goal, of course, is a better fundamental understanding of rubberlike elasticity. Siloxanes are useful in such work because cross-links can be introduced and chain lengths determined in a carefully controlled manner by applying various cure chemistries. Stress-strain isotherms in elongations up to rupture and equilibrium swelling behavior have been investigated (18,426).

Silicone polymers are electrical insulators. The dielectric constant is ca 2.7 at  $25^{\circ}\text{C}$ . Ozone and corona resistance is excellent, approaching that of mica in some cases (342,388).

The overall weatherability of silicone elastomers is exceptional. Samples exposed to outdoor weathering for 15 years have shown no significant loss of physical properties (342).

Fully cured rubber has no odor or taste. It is not toxic and can be formulated for physiological inertness (341–343).

The properties of silicone elastomers as they are important to various classes of applications are presented in Table 22 (67,378–388,427).

Silicone use is sometimes restricted by tear strength, abrasion resistance, or other considerations. In interpenetrating networks the inclusion of silicones with crystalline organic thermoplastic materials improves mechanical strength. This technology is used for Rimplast, where a hydrosilation-curing silicone is vulcanized within the organic matrix (173,428).

### Economic Aspects

The four principal U.S. manufacturers of silicones include Dow Corning, General Electric, Union Carbide, and Wacker Silicones (formerly Stauffer-Wacker and SWS Silicones); large producers are also found in the UK, France, the FRG, the GDR, Japan, and the USSR, and small manufacturers in Belgium, Italy, Czechoslovakia, and elsewhere (173,429).

Worldwide production of silicones was estimated at  $4.5 \times 10^5$  t annually in 1986, with the United States accounting for approximately half of the total. Average U.S. prices (1981–1986) of \$3–6/kg for fluids and resins and \$6–9/kg for elastomers imply that total worldwide sales are now over three billion dollars annually (430). Accurate statistics on production volumes of silicone materials

Table 22. Properties of Silicone Elastomers Pertaining to Applications\*

Application	Thermal stability	Compression set	Flammability characteristics	Electrical resistivity	Corona resistance	Low temperature flexibility	Chemical inertness	Biological inertness	Rapid or low temperature cure	Solvent resistance	Adhesion to glass and metals	Durability to weather and aging
electrical insulation	X	X	X	X	X	X			X			X
aircraft seals	X	X	X			X	X	X		X	X	X
underwater seals		X										
electronic encapsulants	X		X	X	X		X		X		X	X
mechanical components	X	X				X				X	X	X
construction materials			X			X		X	X		X	X
thermal protection	X		X			X	X		X		X	X
consumer and personal uses				X			X	X	X		X	X

\* Refs. 67, 378-388, and 427.

are frequently proprietary and difficult to obtain. Product lines are diverse, and producers vary in their marketing emphasis.

Silicone production has increased markedly over the years. Worldwide production in 1950, estimated at  $10^3$  t, rose to near  $10^5$  t in the mid-1970s; growth continues to be strong. Projected annual growth rates through the early 1990s are expected to be around 10% in the United States and Japan and greater in Western Europe. Typical prices for basic silicone fluids (dimethylsilicone oils) were around \$11/kg in 1950 and under \$5/kg in 1970 and are now on the order of \$3/kg in bulk (173). This price history, in the midst of inflation, reflects impressive productivity gains, which have opened new market areas through cost competitiveness with other, often inferior, organic-based materials. More importantly, a steady flow of process innovations and new product technologies has continued throughout this time. Any initial premiums charged for silicones are offset by superior properties, performance, and service life.

Silicone products include fluids (50–55 wt %), resins (5–10 wt %), and elastomers (40–45 wt %) (173). Other products, eg, emulsions, greases, pressure-sensitive adhesives, and dispersions, are derived from these three basic types. Organosilanes, of growing importance, are listed as fluids, chemicals, or silanes by most producers.

Over 1000 different silicone products are commercially available. The main producers supply a large number of equivalent grades, but each producer also offers certain products that are particular to production capability and marketing strategy. Generic product names are common, eg, silicone fluid, silicone rubber, etc. Trade names include Versilube lubricants and Silglaze construction sealants (General Electric) (300,382) and Dri-Sil concrete and masonry treatment, Molykote specialty lubricants, and Syl-off coatings (Dow Corning) (251).

### Analysis and Testing

The analytical chemistry of silanes, silicone oligomers, and polymers reflects the uniqueness of silicon and its influence on the bond properties in these structures (432–434).

Mass spectrometry and gas chromatography are widely used to identify and measure volatile silicones and silane intermediates (35,435–438). A recent study used high resolution capillary chromatographic analysis with retention index mapping as well as mass spectrometry to identify approximately 40 oligomer components in a mixed siloxane copolymer (439). Liquid and gel-permeation chromatography have been used to determine the distribution of molecular weights in silicone polymers (440) and as preparative techniques for molecular weight fractions (441). Molecular weights can be determined by intrinsic viscosity measurements or, in the case of linear polymers, from the bulk viscosity. Standard techniques of fractional precipitation are widely used for measuring molecular weight distributions.

Ir and uv spectroscopy are useful for establishing the chemical composition. The ir siloxane or other absorption bands may be used to determine the silicones or silicates in a mixture. Uv spectra are useful for phenyl- and vinyl-coating siloxanes; some groups, such as silanols, are most readily observed in the near-



ir region. Silicones are identified and determined by means of their ir (442) or uv spectra: the  $-\text{SiCH}_3$  and  $-\text{SiCH}_2\text{CH}_3$  groups absorb at 1259 and 800  $\text{cm}^{-1}$ , respectively, and  $\text{Si}-\text{O}-\text{Si}$  at 1010–1110  $\text{cm}^{-1}$ . The ratio of methyl to phenyl groups is determined by measuring the intensity of  $-\text{SiCH}_3$  and  $-\text{SiC}_6\text{H}_5$  bands at 1263 and 1435  $\text{cm}^{-1}$ , respectively (443). Phenylsilicones also absorb at 260, 265, and 272 nm in the uv;  $\text{Si}-\text{H}$  is determined by ir absorption at 2100–2250  $\text{cm}^{-1}$ . The methyltriacetoxysilane concentration in continuously compounded RTV sealants is monitored on-line by automated laser-ir spectroscopy (402).

Nuclear magnetic resonance spectroscopy of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  is an important tool for the analysis of organosilicon compositions. Advances in silicon-29 spectroscopy, for example, are providing a new capability for elucidating the structural elements in complex siloxane networks (444,445).

Special groups are determined by specific chemical reactions. For example, chlorosilanes are hydrolyzed, and the halogen is determined by titration with alkali or silver nitrate. Other types of halogen substitution may require more drastic methods of decomposition. Silicon hydride ( $\text{Si}-\text{H}$ ) is assayed by determination of the hydrogen evolved upon base-catalyzed hydrolysis or alcoholysis. Silanol can be determined by measuring the methane evolved with methyl Grignard reagent; water is corrected for by reaction with calcium hydride, which, unless specially prepared, does not react with silanol. Water and silanol can also be determined separately by ir techniques.

In paper, textiles, or formulations, silicones are quantitatively determined by ashing and determination as silica by atomic absorption methods or by extraction with solvents and measurement of ir absorption.

Thermal stability, highly significant in silicone evaluation, is monitored by thermogravimetric analysis; often assisted by dta. Since environmental factors and chemical neutrality affect performance at high temperatures, oven-aging tests on finished products are frequently required. Measurement of weight loss on heat aging is frequently more sensitive than direct chemical methods for detecting the presence of trace amounts of strong acid or base, which reduce polymer stability.

A great variety of analytical techniques have been applied to silicone processing and quality control. In the early days of commercial production, the composition of chlorosilane intermediate mixtures was determined by analytical distillation and weight determination of fractions, supplemented by wet analysis of hydrolyzable chlorine and specific gravity measurements. These methods were soon superseded by mass spectrometry, which was displaced by gas chromatography, the technique currently preferred. Gas chromatography is also used to monitor alkoxy- and acyloxysilanes and the lower boiling linear and cyclic siloxanes. On-line (in-process) monitoring of continuous and semicontinuous processes employs these and other relevant techniques.

Quality control testing of silicones utilizes a combination of physical and chemical measurements to ensure satisfactory product performance and processibility. For example, in addition to the usual physical properties of cured elastomers, the plasticity of heat-cured rubber and the extrusion rate of RTV elastomers under standard conditions are important to the customer. Where the

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silicone application involves surface activity, a use test is frequently the only reliable indicator of performance. Thus, for antifoaming agents, measurement of foam reduction upon addition of the silicone emulsion to an agitated standard detergent solution may be employed. The product data sheets and technical bulletins of producers of commercial silicones can be consulted (251,300,301,378, 379,381-387).

### Environmental Aspects

Silicones are generally considered nonhazardous (446,447). Many of the raw materials and intermediates, however, are hazardous substances with the potential of an adverse impact on the environment, if not properly handled. The principal raw materials for organosilane manufacture are silicon metal, copper (catalyst), methyl chloride, methyl alcohol, and hydrogen chloride. Significant quantities of chlorobenzene, vinyl chloride, and acetic acid anhydride are also used. Organic solvents such as toluene, xylenes, acetone, isopropyl alcohol, and aliphatic hydrocarbons are needed for processing. Manufacture of a commercial product requires integrated high volume continuous systems and finishing and packaging operations.

Silicone manufacture thus produces a collection of wastes, including residues and by-products, for disposal; related wastewater streams require treatment prior to discharge (446).

Most solid and liquid wastes and process vent gases can be incinerated. Combustion of silicones gives nonhazardous products, mainly water, carbon dioxide, and silica particulates; combustion of chlorosilanes evolves HCl. The incineration product gases need water scrubbing before release into the environment. These waters remove the particulates and HCl and can be acidic.

Other process wastewater streams, eg, from decantations, washings, and vent scrubbers, are often highly acidic. Hydrochloric acid, the main by-product of silicone manufacture, is produced in large amounts. Neutralization of this acid gives large quantities of dissolved chlorides. These waters also contain various organic compounds and silicones.

Copper is removed from wastewaters by alkaline precipitation. Complete removal seems difficult and may be hindered by high dissolved solids concentrations (446).

Comprehensive wastewater treatment involves a combination of steps that include neutralization, precipitation, clarification, and some means of removal of organic materials. Air stripping with incineration of the resulting off-gases is one possibility. Biological treatment is applicable in some circumstances. Residual silicones (oils) are removed by skimming (446); solids recovered by clarification are mostly silica.

Pollutant discharges have been substantially reduced by U.S. silicone manufacturers in the years since 1976, while silicone production has increased more than 200%. Overall discharges to surface waters have decreased by 99% for methyl chloride, 84% for copper, 53% for biological oxygen demand, and 12% for total dissolved solids. This performance has been consistent with the goals of the Clean Water Act (446).

Certain solid wastes from the silicone industry are nonhazardous, including scrap elastomer compounds and resins. Spent reaction bed powders from the direct process can be deactivated before disposal (448). Waste chlorosilanes, including direct-process residues and slurries, form easily disposable gels upon hydrolysis (438); copper can be removed from the hydrolyzed residues (449). Effective containment and cleanup procedures for silicone fluids are available (447,450).

The behavior of liquid polydimethylsiloxanes released into the environment has been investigated (451-454). Silicone oils are not significantly biodegraded and do not appear to bioaccumulate (447), nevertheless, their persistence is limited. In the natural environment liquid methylsilicones can be subject to complete degradation, into water, carbon dioxide, and silica or inorganic silicates.

Degradation occurs at surfaces. Thin-film formation appears to be a necessary prerequisite. Surface areas tend to maximize as releases disperse in the environment. Water is generally available. Siloxane bonds are attacked hydrolytically to form smaller cyclic or silanol-functional molecules. Clays present in many soils can serve as catalysts. As the molecules become smaller in size, the silanol-functional species become more water soluble and cyclic species more volatile. Eventually, the silanol products are completely miscible with water; they may also form salts and undergo other reactions.

Another degradative route involves the oxidative removal of methyl groups. Hydroxyl radicals (not ions) are formed in an aquatic situation by the reaction of water with atomic oxygen. Nitrate ion and ozone are potential sources of this atomic oxygen. Hydroxyl radicals may also be present in moist airborne situations. They can attack Si—C bonds, forming Si—O bonds and liberating carbon compounds in the methane oxidative series.

Hydrolytic degradation is much faster than ambient oxidative degradation. A thin film of silicone oil on water might disappear in days (447). Volatile dimethylsilicones appear to have considerable stability toward autooxidation in the atmosphere.

### Health and Safety Factors

Polydimethylsiloxanes generally are not linked to harmful physiological effects. Higher molecular weight polymers appear to be biologically inert and are nonmetabolizable. They do not show toxic behavior, cause blood coagulation, or adhere to body tissues (455,456). Even long-term studies have found no evidence of carcinogenicity or adverse reproductive organ effects. These properties result from the molecular weight, incompatibility, and stability of the polymers (12,67). Lower molecular weight materials may be biologically absorbed and have a very low order of toxicity. Polydimethylsiloxanes cause some temporary eye irritation (457).

Most silicone rubber compounds are not considered hazardous. Silicone rubber is resistant to bacterial or fungal growth. Bacterial growth has been noted in a few cases, probably caused by nonsilicone components in the composition, such as fatty acids (458,459).

The harmless character of the methyl polymers is shared by alkyl-, fluoroalkyl-, and phenyl-substituted polymers. Certain low molecular weight oligomers from this group are known to be biologically active. The compound *cis*-2,6-

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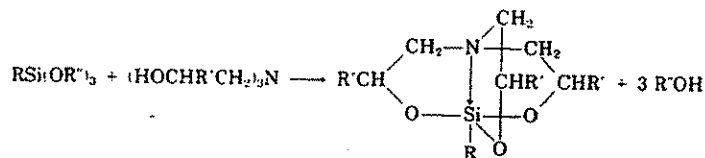
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diphenylhexamethylcyclotetrasiloxane, a notable example, is an active estrogen and has been used as an antifertility agent and for prostate cancer treatment. Methylphenyl and methyltrifluoropropyl trimers and tetramers are biologically active (12,49,456,460-462).

Formulated silicones may contain ingredients that can be irritating or toxic. Some of the metallic or organometallic catalysts present in resins or RTV rubbers in small amounts are irritating or toxic; by-products of elastomer cure may be irritating. Emulsifiers or bactericides used to stabilize silicone elastomers are potential hazards. Many such products, however, are formulated to meet specific safety standards. The solvents employed for silicone resin solutions may be irritating or flammable.

Reactive organosilicon compounds used in product formulations may be slightly toxic (457,463,464). For example, methyltriacetoxysilane and ethyl orthosilicate are used in small amounts in RTV elastomers; they are consumed by curing. Oxidative thermal degradation can lead to the formation of formaldehyde and phenol (10). Trifluoropropyl silicones form toxic materials above 280°C (465). Thus, even though silicone polymers are generally without adverse physiological effects, the same cannot be assumed for all silicone products under all conditions.

Some simple organosilicon compounds show varying degrees of biological activity; for example, hexamethyldisiloxane has toxic properties similar to those of many solvents; trimethylsilanol is a central nervous system depressant; and trimethoxysilane affects the eyes (12,456,464). So-called silatranes are also of interest in this regard. These compounds are pentacoordinate, cyclic "tritych" complexes formed, for example, by the reaction of trialkoxysilanes and trialkanolamines:



The aromatic silatranes (R = aryl) are highly toxic. Less toxic derivatives are being evaluated as healing agents (6,466,467).

Chlorosilanes are hazardous chemicals and should be treated as strong acids because of the HCl liberated on hydrolysis. Silicon tetrachloride is nonflammable, but the organochlorosilanes are flammable. Closed-cup flash points are -28°C for (CH<sub>3</sub>)<sub>3</sub>SiCl and -9°C for CH<sub>3</sub>SiCl<sub>3</sub>. Volatile oligomeric siloxanes, formed by decomposition of the polymers, are slightly flammable. On hydrolysis or alcoholysis compounds containing Si-H liberate hydrogen, which is a hazard in terms of both flammability and generation of pressure (457). All these materials can accumulate static electrical charges (66).

### Applications

Silicones are widely used in industry and consumer products. Applications are based on properties and cost effectiveness. Savings in assembly, installation, and labor costs, combined with longer service life, offset any price premium initially charged for silicones. Some applications require unique properties of

silicones not offered by other materials. Salient properties of dimethylsilicones include thermal and oxidative stability; little dependence of physical properties on temperature; resistance to weathering, ozone, and radiation; low surface tension; high surface activity; good spreading power; and chemical and biological inertness (67).

Silicone chemistry permits a wide range of product development. Varying the molecular structure or formulation ingredients often results in dramatic differences in product performance. Some methylsilicone compositions are adhesives, whereas others act as release agents. The properties of dimethylsilicones are modified by substituting phenyl, vinyl, or longer-chain alkyls for methyl. Some methylsilicone fluids function as defoamers, whereas similar fluids containing polyether groups are used as surfactants to regulate foam pore structure (3,4,10,67).

Silicones are used as engineering materials and are incorporated as components or additives in many other compositions. Articles fabricated from heat-cured silicone rubber retain physical and electrical properties over a broad temperature range, from -100 to 250°C. Silicones improve the flow, surface structure, and impact resistance of thermoplastic and thermoset resins and prevent the separation of pigments in paints.

The range of silicone applications is extremely wide, as shown below:

#### *Fluids*

plastic additives	greases
hydraulic fluids	coagulants
vibration damping	particle and fiber treatments
release agents	cosmetic and health product additives
antifoamers	heat-transfer media
dielectric media	polishes
water repellence	lubricants
surfactants	

#### *Resins*

varnishes	electrical insulation
paints	pressure-sensitive adhesives
molding compounds	laminates
protective coatings	release coatings
encapsulants	adhesives
junction coatings	

#### *RTV rubbers*

sealants	encapsulants
adhesives	electrical insulation
conformal coatings	glazing
gaskets	medical implants
foams	surgical aids
molding parts	mold making

#### *Heat-cured rubbers*

tubing and hoses	autoignition cable and spark-plug boots
belting	extruding
wire-cable insulation	medical implants

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penetration seals  
molded parts  
embossing-calendering rollers

laminates  
electrically conducting rubber  
fabric coating  
foams

Many silicone products are covered by military and federal government specifications (Table 23). The American Society for Testing and Materials (ASTM) has set standards and test methods for silicone fluids (ASTM D2425 and D4283), silicone gels (ASTM F881), silicone elastomers (ASTM D2934), silicone polymers (ASTM D3733), and silicone-modified alkyds (ASTM D3733).

**Table 23. U.S. Military and Federal Government Specifications for Silicones**

Product	Specification
rubber compound	MIL-S-8660
encapsulant	MIL-S-83384
fluid	
dimethyl	AMS <sup>*</sup> -2329
chlorinated phenyl	MIL-S-8187
resin coating	AMS-3135
rubber	
RTV	AMS-3362
	AMS-3364
	AMS-3365
	AMS-3366
	AMS-3367
low temperature	AMS-3332
sheet	AMS-3315D
heat resistant	AMS-3320E
oil resistant	AMS-3356C
sponge	AMS-3192
	AMS-3194A
	AMS-3195C
	AMS-3196C

<sup>\*</sup> Aeronautical materials specification.

In medical and surgical applications silicone fluids are used in gastric disorders (as antifatulents). Treatment of wound dressings with silicone fluids prevents sticking. Silicone fluids improve the stability and drainage of medicine bottles. Plasma bottles are treated to avoid blood coagulation and prevent the blood from wetting the bottle, facilitating draining. Rubber parts are used for surgical tubing, and RTV rubber is used as a dental mold material. Medical-grade elastomers are used for heart valves, prosthetic parts, and contact lenses (qv). RTV materials are used to encase pacemakers and to coat catheters. The Dow Corning Center for Aid to Medical Research, founded in 1959 in Midland, Mich., is a valuable source of information on medical and surgical uses for silicones (468,469).

Siloxane oligomers and fluids are used in cosmetic applications. Antiperspirant and deodorant formulations contain volatile oligomers to provide a mois-

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ture barrier. Such products do not feel oily or sticky. Silicones in skin creams and lotions provide softness and smoothness and prevent the soaping of other ingredients. Hair products made with silicone fluids facilitate handling and provide sheen without an oily feeling (67,173).

In the electrical and electronics industries, silicone fluids are used as dielectric media in transformers, resins for molding compounds to make enclosures, heat-cured rubber for wire and cable coatings, and RTV silicone encapsulants to protect delicate circuitry.

Applications in the automotive industry include silicone fluids as working liquids in hydraulic brake systems, gels for shock-absorbing devices, and RTV sealants for windshield installations; RTV silicone rubber is also used in automated gasket-forming operations, in which a bead of silicone is dispensed directly on parts, eg, axle covers, window seals, taillight assemblies, and engine-oil pans.

In construction, RTV silicone sealants are used in glazing (including structural glazing), sealing, and caulking applications (470). Sprayed-on roofing systems include a silicone rubber coating over polyurethane or another base material. In concrete and masonry, silicones improve water repellence and environmental protection.

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**SILICON POLYMERS.** See POLYSILANES AND POLYCARBOSILANES; PRECERAMIC POLYMERS; SILICATES; SILICONES.

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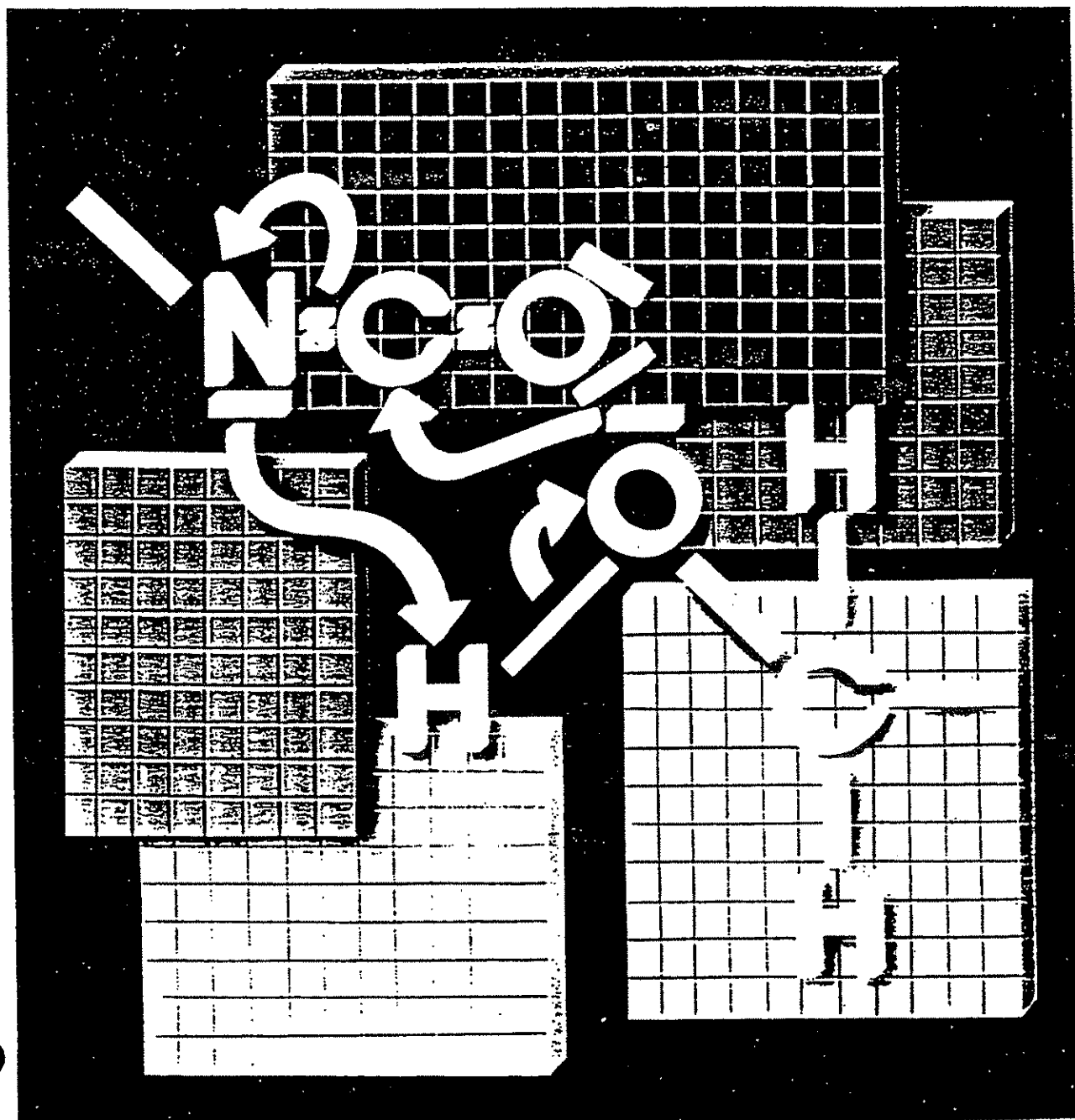
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# The Chemistry of Polyurethane Coatings

Mobay Corporation  
A BAYER U.S.A. COMPANY

Bayer

## A General Reference Manual



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Mobay Raw Materials for Urethane Coatings

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## I. Introduction

During the late 1930s, Otto Bayer and co-workers pioneered the chemistry of polyisocyanates, a technology which led to the advent of polyurethanes for a variety of applications. The principle reaction, shown in Figure 1, occurs between an isocyanate and an alcohol to form a urethane. The reaction of difunctional isocyanates with difunctional alcohols leads to polyurethanes. However, formation of films with superior resistance to abrasion, chemicals, and temperature extremes requires a three-dimensional, crosslinked structure. This can be readily accomplished with urethane technology by employing at least one reaction partner that contains three or more reactive groups in the molecule. In many applications, both the isocyanate and alcohol reactants in two-component systems are resins that contain multiple functional groups.

Since 1955, Mobay Corporation has introduced a variety of monomeric and polymeric isocyanates, polyesters, polyethers, and acrylics for use in the formulation of polyurethane coatings. Unlike alkyd or melamine systems, polyurethane coatings are based on well-defined stoichiometry. This feature allows the design of urethane systems to meet specific end-use requirements.

This brochure is intended to provide the coatings formulator with background information on the chemistry of one- and two-component polyurethane coating systems. Further information from Mobay Corporation in the form of Product Information Bulletins and applications literature is available through your Mobay representative.

## II. General Information

The isocyanate group can react with any compound containing a reactive hydrogen. The three reactions shown in Figure 1 are of principle interest. Reaction of an isocyanate with an alcohol yields a urethane; reaction of an isocyanate with an amine yields a urea; and reaction of an isocyanate with water will result in a carbamic acid which is unstable and decomposes to yield carbon dioxide and amine. Other potential isocyanate co-reactants include carboxylic acids, urethanes and ureas.

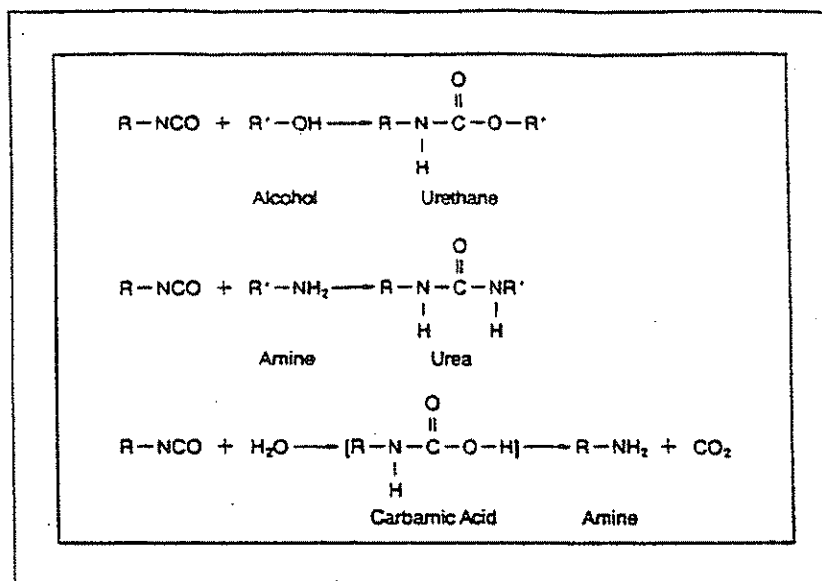


Figure 1: Reactions of the isocyanate group

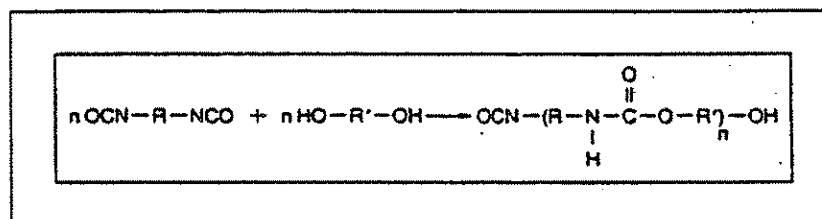


Figure 2: Formation of urethane polymer

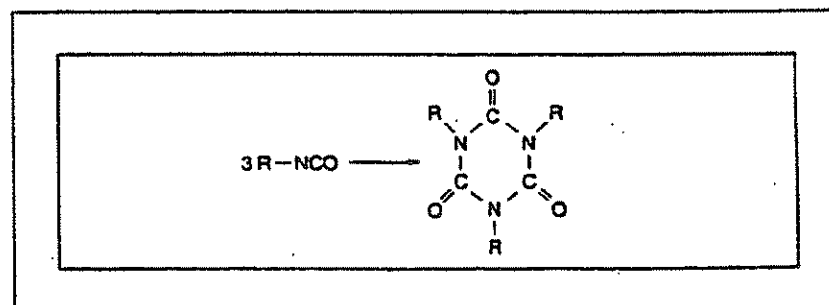


Figure 3: Formation of the isocyanurate ring

In order to prepare polymeric materials, the reaction partners must each have at least two functional groups per molecule (Figure 2). Linear polymers are formed when the reaction partners are each difunctional. Three dimensional networks require that at least one of the reaction partners has three or more reactive groups.

The isocyanate group can also be made to undergo self-condensation. For example, three isocyanates can be trimerized to form the isocyanurate ring as is shown in Figure 3.

### III. Nomenclature

The trade names for the products discussed in this brochure are as follows:

- *Desmodur* and *Mondur*—Aliphatic and aromatic diisocyanate monomers and polyisocyanate oligomers.
- *Desmophen* and *Multron*—Hydroxy functional polyester, acrylic and polyether reaction partners for Desmodur and Mondur polyisocyanates.
- *Desmodur BL* and *Desmotherm*—Blocked polyisocyanates for baking enamels.
- *Desmocap*—Blocked polyisocyanates for room temperature cure.
- *Creelan*—Polyester and blocked polyisocyanate raw materials for thermoset powder coatings.
- *Desmolac*—High molecular weight polyurethane lacquer resins.
- *Baybond*—Aqueous polyurethane dispersions.

Monomeric diisocyanates are major building blocks for the value added products most commonly used in the coatings industry. Mobay's polyisocyanate coatings products are named with nomenclature which stipulates product family, monomeric diisocyanate starting material and weight solids. Familiarity with Mobay's nomenclature will allow a quick determination of the chemical basis for most of Mobay's coatings products. This nomenclature can best be understood by the examples in Tables I and II. For Desmodur E-21, the solids level of 100% is implied. This product designation could also be written as Desmodur E-2100.

As with any system, notable exceptions exist and these relate to the product families of Desmodur N and Mondur CB polyisocyanates (Table III). These long established products predated the attempts toward a systematic nomenclature. Additional details on the nomenclature are contained in the following pages.

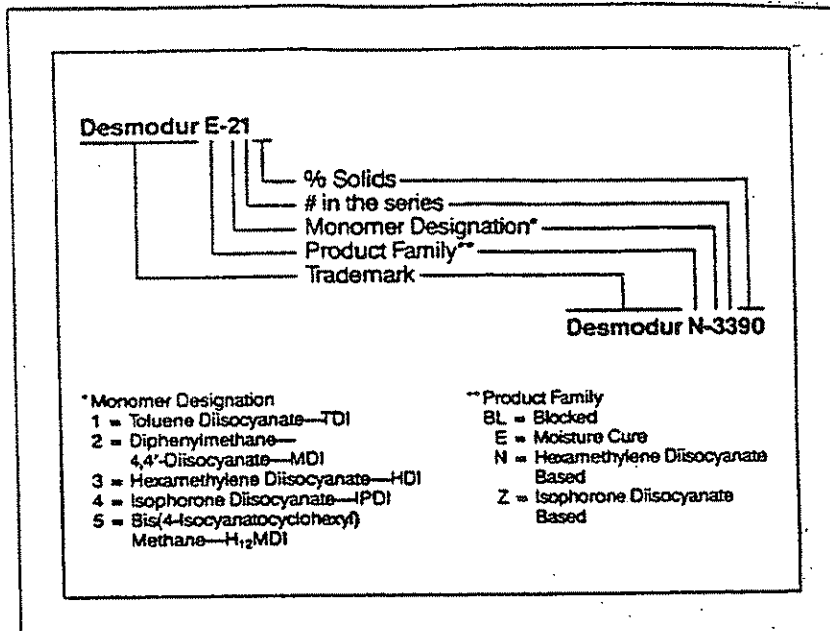


Table I: Nomenclature

Example	Family	Monomer	% Solids
Desmodur E-1361	Moisture Cure	TDI	61
Desmodur E-21	Moisture Cure	MDI	100
Desmodur N-3390	HDI based	HDI	90
Desmodur Z-4370	IPDI based	IPDI	70

Table II: Nomenclature examples

<p>Polyisocyanates based on HDI:</p> <p>Desmodur N-75          Desmodur N-100          Desmodur N-751</p> <p>Polyisocyanates based on TDI:</p> <p>Mondur CB-60          Mondur CB-75          Mondur CB-601          Mondur CB-701</p>
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Table III: Nomenclature exceptions

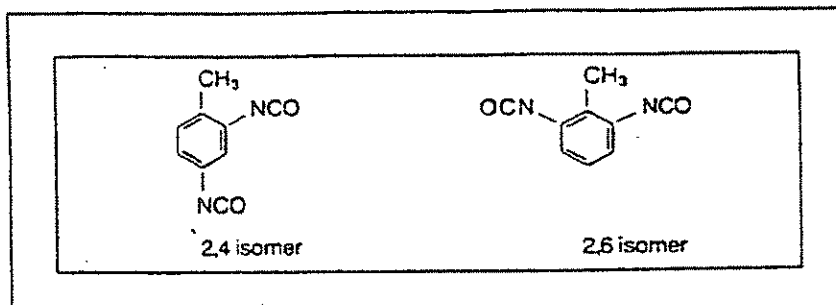


Figure 4: Toluene Diisocyanate (TDI)

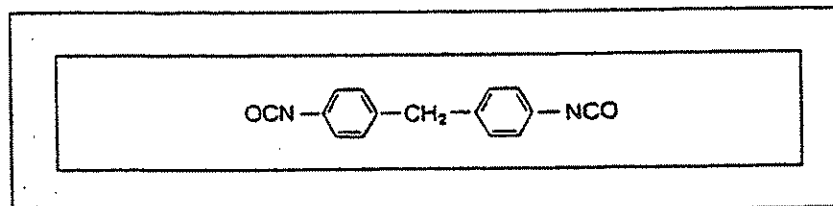


Figure 5: Diphenylmethane 4,4'-Diisocyanate (MDI)

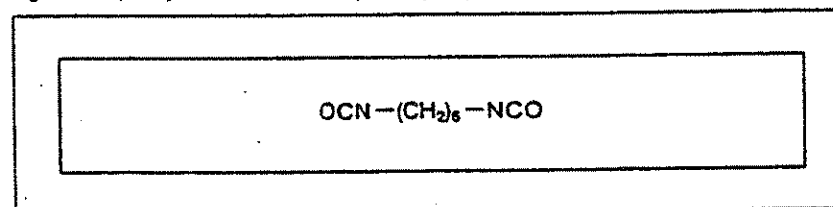


Figure 6: Hexamethylene Diisocyanate (HDI)

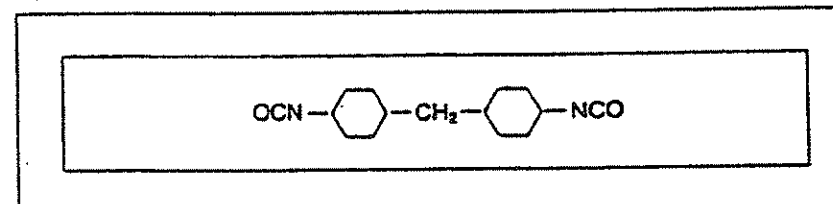


Figure 7: Bis(4-Isocyanatocyclohexyl) Methane

#### IV. Monomeric Diisocyanates

There are important differences between aromatic diisocyanate monomers and aliphatic diisocyanate monomers. The aromatic isocyanate groups are considerably more reactive than the aliphatic isocyanate groups, resulting in coatings that dry faster and develop cure properties faster than comparable systems based on aliphatic isocyanates. Urethane products made from aromatic diisocyanate mono-

mers oxidize more easily than do those prepared from aliphatic diisocyanate monomers, especially when exposed to UV light. The higher resistance of products prepared from aliphatic diisocyanates to UV light-induced degradation means that coatings based on them have better yellowing and chalk resistance than those based on aromatic diisocyanates. The products based on aliphatic diisocyanates are therefore preferred for exterior topcoat applications which require color and gloss retention.

#### Toluene Diisocyanate (TDI):

One of the most important monomers used in the polyurethane industry today is toluene diisocyanate (TDI). In the coatings industry it is used mainly as a raw material in preparing adducts and prepolymers (Section V). TDI is also used as a modifier of alkyd resins. The current method for industrial preparation of TDI produces two isomers, shown in Figure 4. Mobay markets three versions of TDI under the following trademarks:

Mondur TD — 65/35 mixture of 2,4 and 2,6 isomers

Mondur TD-80 — 80/20 mixture of 2,4 and 2,6 isomers

Mondur TDS — 2,4 isomer

Mondur TD-80 is supplied in two different grades varying in acidity.

#### Diphenylmethane 4,4'-Diisocyanate (MDI):

One of the first diisocyanate monomers to achieve widespread industrial use is diphenylmethane 4,4'-diisocyanate (MDI), shown in Figure 5. Mobay markets MDI under the trademark Mondur M and supplies the material as a fused solid, a flaked solid, or a liquid.

#### Hexamethylene Diisocyanate (HDI):

Another important diisocyanate monomer used for the preparation of a wide variety of isocyanate adducts is hexamethylene diisocyanate (HDI), shown in Figure 6. This material is marketed by Mobay under the trademark Desmodur H.

#### Bis(4-Isocyanatocyclohexyl) Methane:

The monomeric diisocyanate shown in Figure 7, bis(4-Isocyanatocyclohexyl) methane, is marketed by Mobay under the trademark Desmodur W.

Desmodur W is also known as hydrogenated MDI (HMDI or H<sub>12</sub> MDI), reduced MDI (RMDI), or saturated MDI (SMDI). It is a useful material for the production of hydrolytically stable polyurethanes as well as prepolymers for one- or two-component formulations, and for cast elastomers.

## V. Polyisocyanates

Industrial hygiene concerns limit the use of monomeric diisocyanates directly in coating applications. Higher molecular weight species, such as adducts, prepolymers and isocyanurate trimers, are preferred because they contain only very low levels of monomeric diisocyanate. A low level of monomeric diisocyanate reduces the concerns associated with manufacturing and handling urethane coatings.

### TDI Based Polyisocyanates:

As mentioned in Section IV, TDI has gained particular significance in polyurethane coatings technology. Two different TDI based polyisocyanate products are marketed by Mobay, a TDI-trimethylolpropane (TMP) adduct and an isocyanurate trimer. The idealized structures are shown in Figures 8 and 9.

The various supply forms of the adduct are marketed by Mobay under the trademark Mondur CB. The trimer is marketed by Mobay under the trademark Desmodur IL.

Both Mondur CB and Desmodur IL can be used in two-component coatings using polyols as coreactants. Desmodur IL is particularly suitable in applications where extremely rapid curing two-component polyurethane coatings are required.

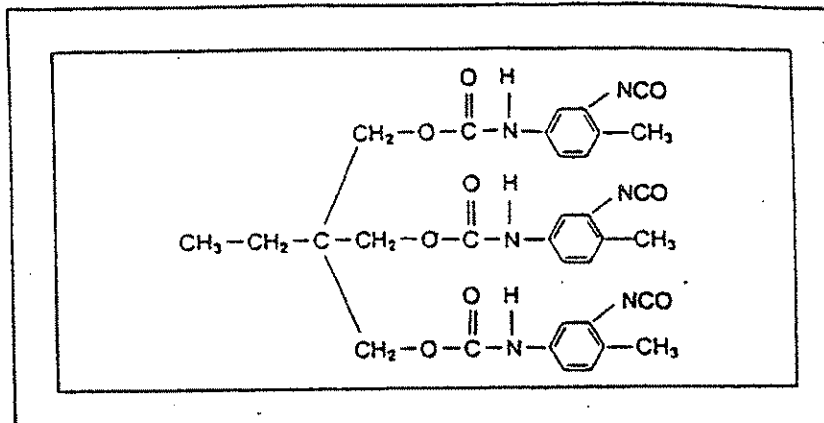


Figure 8: Adduct of TDI and TMP

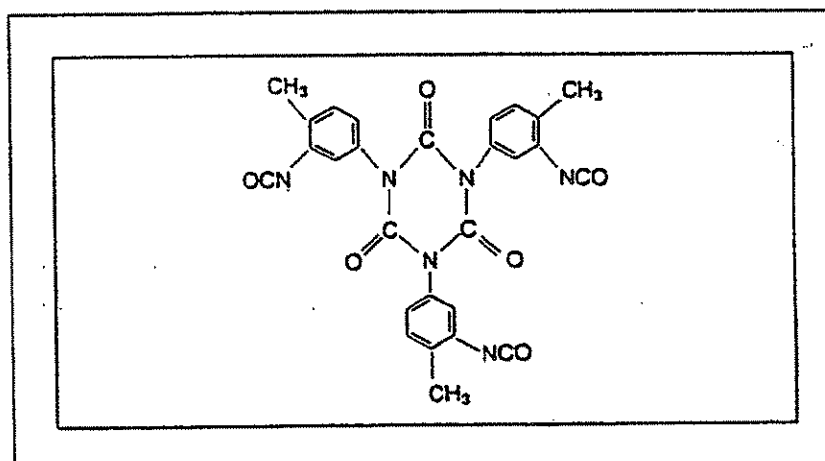
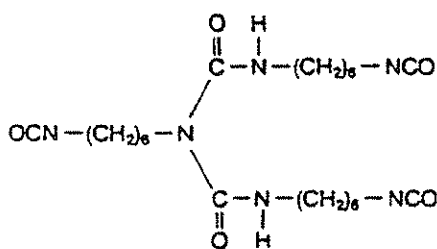


Figure 9: Idealized structure of Desmodur IL polyisocyanate





**Figure 10: The biuret of HDI**

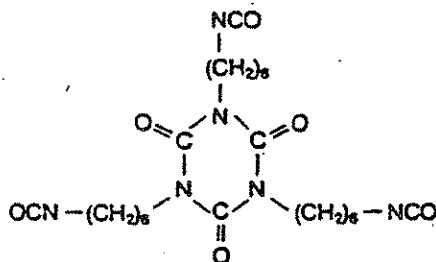
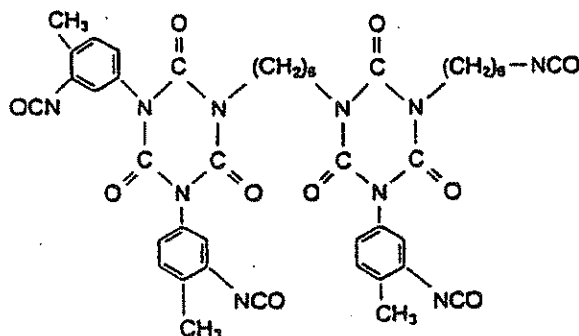


Figure 11: The isocyanurate ring of HDI



**Figure 12: Copolymer of TDI and HDI**

### HDI Based Polyisocyanates:

Polyisocyanates based on HDI represent the most important class of polyisocyanates used today in polyurethane coatings. Coatings prepared with these products have excellent resistance to chemicals and abrasion and superior weathering characteristics, including retention of gloss and resistance to yellowing and chalking.

One commercial class of products includes Mobay's Desmodur N-75, Desmodur N-100 and Desmodur N-3200, which are polymeric materials that contain biuret groups. An idealized structure of an HDI-based biuret is shown in Figure 10. Desmodur N-75 is a 75 % solids version of Desmodur N-100. Desmodur N-3200 is a low viscosity version of Desmodur N-100.

Like TDI, HDI can be converted to a trimer that contains an isocyanurate ring (Figure 11). These products, marketed under the trademarks Desmodur N-3300 and Desmodur N-3390, have better thermal stability and weathering properties than the biuret products. Desmodur N-3300 has a low viscosity similar to that of Desmodur N-3200.

An isocyanurate copolymer of TDI and HDI (Figure 12) is marketed under the trademark Desmodur HL. As expected, the properties of films prepared from Desmodur HL are intermediate between those prepared from the products Desmodur N-3300 and Desmodur IL.

**MDI Based Polyisocyanates:**

In addition to the three forms of Mondur M (monomeric MDI) discussed in Section IV, oligomeric mixtures of the type shown in Figure 13, are marketed under the trademarks Mondur MR, Mondur MRS, Mondur MRS 4, and Mondur MRS 5. These materials, supplied as low viscosity liquids containing no solvent, are used to prepare high solids or solvent-free coatings, caulking, and sealants. Either one- or two-component coatings can be prepared from these polyisocyanates.

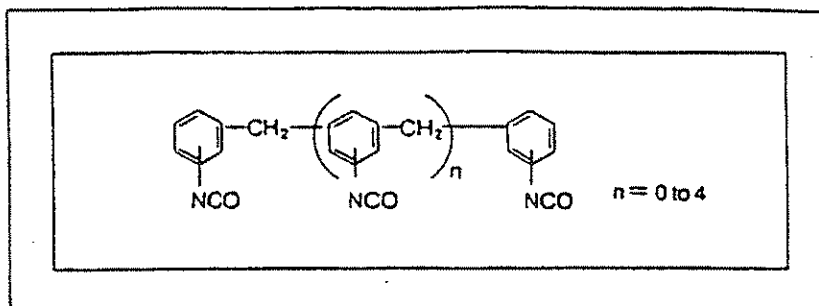


Figure 13: MDI Oligomers

**Isophorone Diisocyanate (IPDI) Based Polyisocyanates:**

Isocyanurate trimers based on isophorone diisocyanate (Figure 14) are marketed under the trademarks Desmodur Z-4370 and Desmodur Z-4370/2. These resins are less reactive than Desmodur N polyisocyanates and produce less flexible films. However, Desmodur Z polyisocyanates are compatible with aliphatic hydrocarbon solvent blends and find use as additives in alkyd systems.

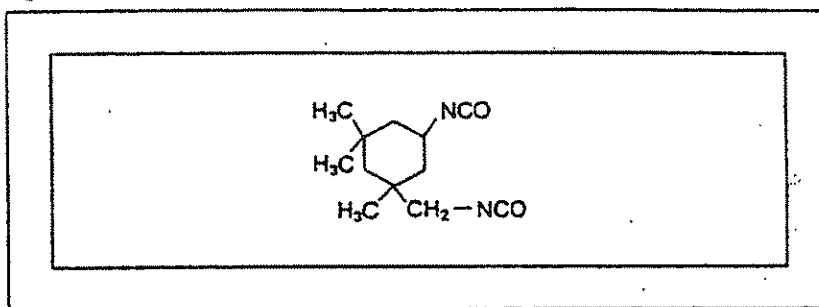


Figure 14: Isophorone Diisocyanate (IPDI)

**Moisture-Curing Polyisocyanates:**

In addition to the many polyisocyanates that may be used in one-component applications, Desmodur E polyisocyanates have been specifically developed for use as moisture-curing systems. The reaction of isocyanate groups with atmospheric moisture forms the basis of this technology. These products are supplied as higher molecular weight polyurethane prepolymers containing reactive isocyanate groups (Figure 15). For a variety of applications, Desmodur E polyisocyanates can be used in the form supplied or as diluted solutions. In addition to moisture-cure systems, these products can be used in two-component formulations.

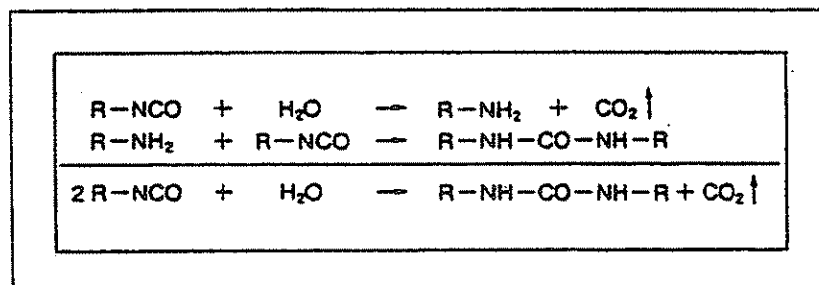


Figure 15: Polyurea Formation

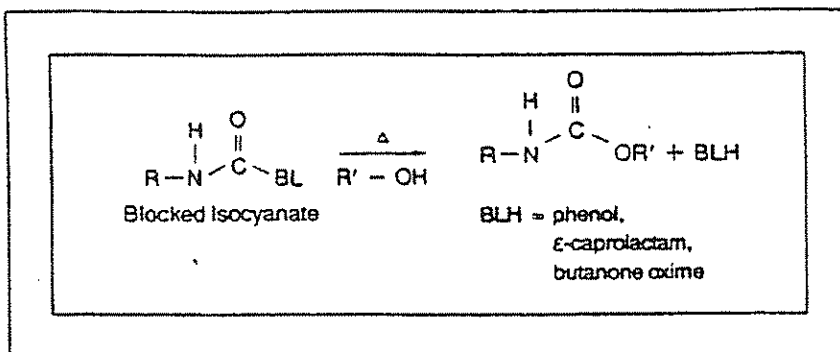


Figure 16: Crosslinking of Blocked Polyisocyanates

### Blocked Polyisocyanates:

The polyisocyanates described thus far contain unreacted isocyanate groups. In typical two-component formulations, these products are usually combined with the polyol just prior to application. When the isocyanate and polyol are mixed, they immediately begin to react with one another which leads to a limited, although usually adequate, potlife. Another group of Desmodur products contains isocyanate groups that are blocked by compounds such as  $\epsilon$ -caprolactam, butanone oxime or phenol. At room temperature, these blocked isocyanates do not react with polyols at any appreciable rate. At elevated temperatures, however, the blocked isocyanate reacts with the polyol liberating the blocking agent (Figure 16), which is volatile and leaves the coating. This means that one-component, room-temperature stable coatings can be formulated with blocked isocyanates and suitable polyol components. Crosslinked polyurethane films can be prepared at temperatures as low as 230°F with properties similar to those of corresponding two-component systems.

A special group of blocked isocyanate products are marketed under the Desmocap trademark. These products have been developed to crosslink at room temperature with aliphatic amines.

Mobay supplies a wide variety of blocked polyisocyanates under the following trademarks:

- *Desmodur BL-1185A* —  $\epsilon$ -caprolactam blocked TDI prepolymer
- *Desmodur BL-1260A* —  $\epsilon$ -caprolactam blocked TDI prepolymer
- *Desmodur BL-3175A* — Butanone oxime blocked HDI isocyanurate

- *Desmodur AP Stabil* — Phenol blocked TDI adduct
- *Desmodur CT Stabil* — Phenol blocked TDI isocyanurate
- *Desmocap 11A* — Substituted phenol blocked TDI prepolymer
- *Desmocap 12A* — Substituted phenol blocked TDI prepolymer

## VI. Polyol Reaction Partners

### Desmophen and Multron Polyols:

A wide variety of polyesters, polyethers, and acrylics containing hydroxyl groups are marketed by Mobay under the trademarks Desmophen (polyesters, polyethers and acrylics) and Multron (polyesters).

Desmophen polyesters are available in grades ranging from highly-branched to linear with either high or low hydroxyl content. In general, the product numbers corresponding to the various grades of Desmophen polyesters are a clue to the structure — the lower the number, the higher the degree of branching. As the number increases, the polyesters become increasingly linear and have a lower hydroxyl content.

Desmophen polyacrylic resins can be differentiated from the polyesters by the "A" designation before the grade number; for example; Desmophen A 160, Desmophen A 365, and Desmophen A 450.

Desmophen polyethers are designated by the letter "U" following the number; for example; Desmophen 500U and Desmophen 1600U.

### Other Reaction Partners:

Oils and alkyds can be used in combination with Mobay polyisocyanates. For example, various short oil alkyds can be used with Desmodur HL and Desmodur IL polyisocyanates. Castor oil which contains hydroxyl groups is a potential reaction partner for Mondur CB and Mondur MR.

Mondur CB and Desmodur N combined with epoxy resins containing secondary hydroxyl groups give films with good adhesion and resistance to aggressive chemicals. Certain phenolic resins also give particularly good water-resistant films when they are combined with Mondur CB polyisocyanates.

Silicone resins with hydroxyl groups also react with polyisocyanates. For example, Baysilone UD resin manufactured by Bayer AG, West Germany, when cross-linked with Mondur CB polyisocyanate at room temperature, produces coatings that maintain their mechanical properties longer, even after prolonged treatment of the films at temperatures as high as 180°C. However, a certain degree of yellowing will occur.

Vinyl polymers containing hydroxyl groups are also suitable reaction partners for Mobay polyisocyanates. Such systems can be used for coating wood and plastic substrates.

Other products which are suitable for use with polyisocyanates include cellulose esters, ketone resins, bituminous coal tar, and bitumen.

eg. wt:

if chemist wants 2 NCO group, how must do? you

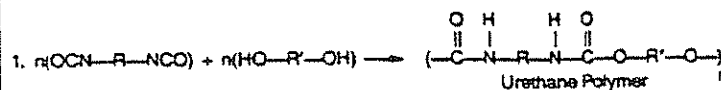
## VII. Two-Component Coating Systems

The most frequently recommended products for two-component applications are Mobay's Desmodur polyisocyanates and Desmophen polyols (DD). In addition, for some applications Mobay's Mondur polyisocyanates and Multron polyesters may also be appropriate. The term DD coating refers to any of the two-component coatings based on polyisocyanates and polyols available from Mobay.

### Calculations:

When preparing two-component coating formulations, the rules for chemical equations are followed. In theory, a maximum molecular weight is reached and those properties associated with molecular weight are optimized when one equivalent of isocyanate reacts with one equivalent of hydroxyl, that is, when the ratio of NCO to OH is 1.0 to 1.0 (Equation 1, Figure 17). In practice, a small excess of isocyanate, about 10%, is often used to allow for the destruction of isocyanate by the likely presence of water in pigments or solvents, so that the NCO to OH ratio of 1.0 to 1.0 is maintained. In addition, it is sometimes desirable to vary the NCO to OH ratio from about 0.9 to 1.0 to about 1.2 to 1.0 in order to modify the properties of the coating. In any event, it is of great importance that the NCO/OH be controlled.

In order to achieve a ratio of NCO to OH of 1.0 to 1.0, the weight of one equivalent of the supplied form of the polyisocyanate is reacted with one equivalent of the supplied form of the polyol. Usually the product literature will list the equivalent weights, but if not, then the polyisocyanate literature will give the % NCO and the polyol literature will give the % OH or the OH value. The NCO equivalent weight can be calculated from the % NCO (Equation 2, Figure 17); and the OH equivalent weight can be calculated from either the % OH or the OH value (Equation 3, Figure 17). These equations can be combined to calculate the weight ratios of ingredients for any NCO/OH. Basic algebra is all that is necessary for these basic manipulations. Sample calculations are shown in Figure 18.



$$2. \text{Equivalent weight (Isocyanate-containing resin)} = \frac{42 \times 100}{\% \text{ NCO}}$$

$$3. (a) \text{Equivalent weight (Hydroxyl-containing resin)} = \frac{17 \times 100}{\% \text{ OH}}$$

$$(b) \text{Equivalent weight (Hydroxyl-containing resin)} = \frac{56,100}{\text{OH Number (OH Value)}}$$

Figure 17: Equations for polyisocyanate/polyol reaction

Determine the amount of Desmodur N-100 polyisocyanate required to react with 300 lbs of Multron R-221-75 polyol. Use a 1.2 to 1.0 NCO to OH ratio.

Desmodur N-100 contains 22% NCO  
Multron R-221-75 contains 33% OH

$$a) \text{Equivalent weight of N-100} = \frac{42 \times 100}{22} = 191$$

$$\text{Equivalent weight of R-221-75} = \frac{17 \times 100}{33} = 515$$

For the theoretical reaction, it is necessary to use 1 equivalent or 191 lbs of N-100 with 1 equivalent or 515 lbs of R-221-75.

$$b) \text{The number of equivalents in 300 lbs of R-221-75} = \frac{300}{515} = 0.58$$

$$c) \text{At 1.0 to 1.0 NCO to OH ratio, equivalents of N-100 required are 0.58.} \\ \therefore \text{The amount of N-100} = 0.58 \times 191 = 111 \text{ lbs}$$

$$d) \text{Since a reaction ratio of 1.2 to 1.0 of NCO to OH is desired, then the amount of N-100 required is } 0.58 \times 1.2 \times 191 = 133 \text{ lbs}$$

Figure 18: Example Problems

### Properties:

The properties of a polyisocyanate/polyol coating depend on certain factors, such as the degree of branching of the reaction partners, the content of reactive groups and the physical state of the individual raw materials.

It is possible to change the film properties by using the same polyisocyanate with different polyols while maintaining a constant stoichiometric ratio. The higher the hydroxyl content of the particular reaction partner, the harder and the more chemically resistant the resultant films will generally be. A low hydroxyl content normally gives softer and more flexible films.

A further possibility for modifying the film properties is to use the same polyol and vary the quantity of the polyisocyanate. By "undercrosslinking," i.e.,  $\text{NCO:OH} < 1$ , the polyurethane films generally become more flexible though they are less weather-resistant and less resistant to solvents and chemicals. On the other hand, by exceeding the stoichiometric quantity of polyisocyanate, or "overcrosslinking," i.e.,  $\text{NCO:OH} > 1$ , the resultant films tend to be harder and have greater chemical resistance.

### Modifiers:

In addition to the two main components, DD coating systems frequently contain other modifying constituents. These are added to improve specific application properties (levelling agents or thickeners for example), and are normally incorporated in the order of 1-10% of the total binder. For certain applications, it may be best to formulate coatings containing more than 35% modifying binder constituents. In addition to cellulose acetate butyrate, low molecular weight acrylic resins and polyvinyl chloride/polyvinyl acetate (PVC/PVAC) copolymers are suitable modifiers. Coatings prepared from combinations of nitrocellulose and aromatic isocyanates tend to yellow substantially and are predominantly used for primers and as clear varnishes for dark substrates. However, combinations with the aliphatic Desmodur N polyisocyanates do not yellow.

### Solvents:

Suitable solvents for two-component systems include esters, ketones, and ether esters. Possible diluents are aromatic hydrocarbons such as toluene, xylene or

higher-boiling aromatic petrochemical hydrocarbons. Desmodur Z polyisocyanates are compatible with aliphatic diluents. Chlorinated hydrocarbons may be used only in systems that do not contain finely divided metal additives. The choice of solvents and diluents should be evaluated for each coating system.

Should it be necessary to dilute polyisocyanates, special care should be taken when selecting the solvents. Any solvent chosen must not contain hydroxyl groups.

Therefore, alcohols or any solvent contaminated with water should not be used. It is not recommended to dilute polyisocyanates below 35% solids content since precipitation of resins may occur.

The water content of the solvents or solvent mixes for polyisocyanates should not exceed 0.05%. Urethane grade solvents are suitable for polyols, as well as polyisocyanates.

Solvents which contain reactive groups, e.g., amines, should not be used since they react with isocyanate groups.

Regulations and safe handling procedures governing combustible liquids must be observed.

### Pigments and Extenders:

The following inorganic pigments are highly suitable:

- White:  $\text{TiO}_2$  types
- Yellow: Iron oxide yellow types, nickel and chrome titanates, light yellow types, chrome yellow and cadmium types
- Brown: Iron oxide brown types
- Red: Iron oxide red pigments, cadmium types
- Black: Iron/manganese mixed metal oxide black, iron oxide black types (not for grey shades) and some carbon blacks
- Blue: Light blue and chrome oxide green types

A marked reduction in the potlife may be expected by using the following pigments: zinc oxide, red lead, lead cyanamid, molybdate red and some carbon blacks. Zinc and lead chromates, as well as zinc phosphate, have gained special importance as passivating pigments for corrosion protection in primers. However, these pigments are only suitable if they do not excessively shorten the potlife. Zinc dust may be used for anti-corrosion

primers as well as non-leaching aluminum for barrier type primers.

The following organic pigments are suitable:

- Blue: Phthalocyanine blue types
- Green: Phthalocyanine green types
- Red: Perylene types and quinacridone types

Organic pigments may catalytically accelerate the curing reaction. Their suitability is best established by testing the potlife. For organic pigments, normally not more than approximately 6%, calculated on solid binder, should be used for glossy films. Note that organic pigments will not always give sufficient coverage in single-coat applications.

In addition to transparent pigments, soluble dyestuffs can also be used to obtain transparent shades. Soluble dyestuffs do not generally have the same light fastness as suitable organic pigments. Metal complex dyestuffs can also be used.

Conventional extenders are barytes, heavy spar, microtalc, kaolin, micaceous iron oxide, magnesium mica, asbestos flour, quartz flour, powdered slate, and silicon carbide. It is advisable to carry out evaluations prior to use.

### Matting Agents:

The incorporation of conventional matting agents based on silica allows any desired level of gloss to be obtained, either with clear or pigmented DD coating systems. Incorporating polyolefin wax is also advantageous. Micronized polypropylene waxes can be incorporated without difficulty and improve the appearance of the matted surface. In the case of readily dispersible products, it is sufficient to mix them simply by high-speed stirring.

To obtain a matt or eggshell gloss effect, 4-15% matting agent, calculated on binder, is generally required. This quantity will vary, depending on the composition of the polyol solution or mill base.

The flattening effect can often be assisted by the incorporation of components which increase the viscosity and/or improve physical drying.

**Levelling Agents:**

Apart from the choice of solvents, the addition of suitable levelling agents can improve the flow properties when necessary.

Cellulose acetate butyrate or low molecular weight acrylic resins, depending on compatibility, are used in quantities of about 0.2-2%, calculated on solid binder.

Nitrocellulose also has the effect of improving the flow and promoting pigment wetting. However, because of the pronounced yellowing in connection with aromatic polyisocyanates, nitrocellulose can only be used with these materials in applications where light stability is not important.

Polyvinyl acetate, polyvinyl butyral, copolymers of PVC/PVAC, as well as certain urea resins, may improve levelling properties. The added quantities are usually between 0.5% and 3%, calculated on the binder. Silicone fluids or fluorochemical surfactants lower the surface tension to improve flow.

**Thickening Agents:**

Certain application methods, such as curtain coating, require increased viscosity of the DD coating. Suitable thickening agents are copolymers of vinyl chloride and vinyl acetate, polyvinyl butyral, nitrocellulose, silicas, thickeners of bentonite and hydrogenated castor oil.

If an increase in the viscosity is desired, copolymers of vinyl chloride and vinyl acetate and polyvinyl butyral can be added to the polyol solution in quantities of 5-10%, based on binder.

Nitrocellulose can be added in quantities of 5-10%, based on polyisocyanate/polyol, resulting in an appreciable increase in viscosity. One disadvantage, however, can be the pronounced yellowing effect when combined with aromatic polyisocyanates.

Hydrogenated castor oil will produce thixotropy, which allows thick films to be applied even to vertical surfaces. Additions of 1% based on resin solids are often sufficient.

Silicas increase the viscosity and also produce thixotropy. An addition of 3% is often adequate and has only a minor influence on the degree of gloss. These products are best suspended with solvents in a dissolver before use.

Bentonite thickeners are used in additions of up to 1.5% on solid binder to prevent the settling of pigments and extenders. These agents are also best suspended with solvents before use.

When selecting thickeners, their compatibility with polyols must be considered. Furthermore, additions that impair the characteristic properties of the coatings must be avoided. This particularly applies to coatings based on Desmodur N polyisocyanates.

**Air Release Agents:**

Air release agents are particularly useful for the prevention of blistering during application by brush, curtain coating or roller coating. Special copolymers of acrylic esters (Modiflow, Monsanto) have proven to be suitable. Although these products are often incompatible with DD coating materials, the slight turbidity which can be observed in the unpigmented coatings is no longer noticeable in the dry film if the correct amount is added. The addition should be a maximum of 0.05% based on solid binder.

**Catalysts:**

Catalysts are used in DD coating systems to shorten the curing time, especially in systems containing aliphatic isocyanates. They differ considerably in the extent to which they accelerate the reaction. Desmorapid PP, a tertiary amine, is often a suitable catalyst. Various metal compounds are also suitable. Dibutyltin dilaurate or zinc octoate, for example, are of particular significance in combination with Desmodur N aliphatic polyisocyanate products or in moisture-curing one component coatings. While accelerating the cure, the use of a catalyst will also shorten the potlife.

The required addition level and effectiveness of a catalyst will vary. An excessive amount of catalyst may impair the development of film properties such as hardness, abrasion resistance, UV resistance and appearance of the film. It is advisable to carry out evaluations prior to making a choice.

**Curing:**

Curing of the DD coating systems can be carried out at room temperature. The drying times can vary considerably depending on the types of polyisocyanate used. The choice of the polyol to be reacted with a polyisocyanate will also affect the system's dry time. In general, systems based on the following polyisocyanates dry at room temperature in these approximate relative times.

Desmodur IL polyisocyanate	1
Desmodur HL polyisocyanate	2
Mondur CB polyisocyanates	6
Desmodur N polyisocyanates, with catalyst	6
Desmodur N polyisocyanates	30

The reaction between the polyisocyanate and polyol can occur at temperatures as low as 32 °F (0 °C) but, in practice, elevated temperatures are often used for forced drying in production line coatings.

The highly reactive Desmodur IL and Desmodur HL polyisocyanates have particular importance for baked finishes as they allow extremely short drying times. Coatings based on Mondur CB or Desmodur N polyisocyanates can also be dried at elevated temperatures in order to reduce the cure time.

Aliphatic polyisocyanates, such as the Desmodur N polyisocyanates, have low reactivity by nature, and longer drying times can be expected. The incorporation of a catalyst such as 0.005 % dibutyltin dilaurate, 0.2 % zinc octoate or 0.5 % Desmorapid PP, on solid binder, reduces the drying time to practical levels.

While Mondur CB polyisocyanate based coatings normally do not require a catalyst, the addition of an accelerator may be advisable for specific applications. Metal-based accelerators have less of an effect on Mondur CB polyisocyanates than the preferred amine based catalysts, e.g., Desmorapid PP. Depending on their effectiveness, additions range between approximately 0.05 % and 0.2 %, on solid binder.

Coatings that are based on Desmodur IL or Desmodur HL polyisocyanates are normally used without a reaction accelerator.

#### Application:

The chemical curing mechanism of DD coatings makes it necessary to consider the following points:

1. Both components *must* be thoroughly mixed together. In some cases it is advantageous to allow the mixture to stand for half an hour before application.
2. The reaction which begins immediately after mixing, results in a gradual increase in viscosity.
3. The increase in viscosity eventually leads to gelation of the paint.

The useable potlife depends on the following factors:

- The binder concentration.
- The NCO/OH ratio.
- The selected polyisocyanate.
- The selected polyol.
- The catalyst type and concentration.
- The temperature of the coating formulation.
- The choice and quality of the solvents.
- The possible effect of any incorporated auxiliaries, pigments, or extenders.

If these facts are taken into account and the coating is properly formulated, the potlife can normally be set to be one working day. In principle, this means that the coating can be applied by any conventional method.

DD coatings can be applied by a variety of methods. Application by spray, brush, conventional roller coating, and curtain coating is possible. Since curtain coating requires relatively high initial viscosity, it is essential that the two-component combination exhibits a slow increase in viscosity at the proper consistency.

Brushable coatings can be formulated by adjustment of viscosity and dry time. Brushable coatings can generally also be applied by airless spraying and in many cases, by the hot-spray method at approximately 110 °F (80 °C). In general, application by the electrostatic spray method is possible due to the polarity of the coatings. Spray coatings applied by the conventional compressed air method require relatively low viscosity and the use of a suitable solvent mix that evaporates as rapidly as possible. Two-component spray guns which automatically meter and mix the components are useful.

Gelation of the remaining portion of the coating, e.g., with dip baths or curtain coating machines, can be delayed by dilution with the amount of polyol required for the next period of work. The required quantity of polyisocyanate should not be added until shortly before recommencing the work. The effect can be made even more pronounced by adding 10 % solvent to the paint mix. Mixing must be done carefully and thoroughly.

A coating which has already been mixed can be kept overnight or during long breaks by chilling or refrigeration. This method can be combined with the procedure described above.

*get this, keep to hand  
for emergency use in  
a 100% pure ball*

### III. Moisture-Curing One-Component Coatings

soluble adducts of diisocyanates or polyisocyanates and polyols with an excess of isocyanate groups ("prepolymers") can crosslink with atmospheric moisture (Figure 19) to give insoluble higher molecular weight polyurethane/polyureas. This reaction describes the curing principle for moisture-curing polyurethane coatings.

There are two ways of formulating one-component coatings of this kind:

- Preparation of prepolymers from suitable polyisocyanates and polyols, or
- Use of Desmodur E polyisocyanates.

#### Prepolymers from Polyisocyanates and Polyols:

Mobay's Desmodur N, Mondur CB and Mondur MRS polyisocyanates are suitable for the preparation of prepolymers for the formulation of one-component coatings. The prepolymers are normally prepared from polyols of low functionality and a stoichiometric excess of isocyanate. A moisture-curing, clear varnish can be made as follows: The polyisocyanate and solvent are mixed for a short time in the dissolver under the exclusion of moisture. If a moisture scavenger is required, para-toluene sulfonyl isocyanate (pTSI) can be added. After this, the polyol, other additives, and if necessary, accelerators, are added and the mixture is packed in a dry, airtight container. The coating reaches its final viscosity after approximately seven days. The storage stability of the final product is dependent on the polyol and should be closely examined.

#### Desmodur E Polyisocyanates:

The name Desmodur E covers a range of ready-to-use, one-component coatings which require no other treatment except for thinning in some cases. Because they are far simpler to use than the two-component coatings, the Desmodur E polyisocyanates have become very popular.

#### Properties:

The properties of moisture-curing one-component coatings are principally determined by the nature of the particular base isocyanate. For example, one-component coatings based on aliphatic isocyanates generally need longer drying times than those based on aromatic isocyanates. The

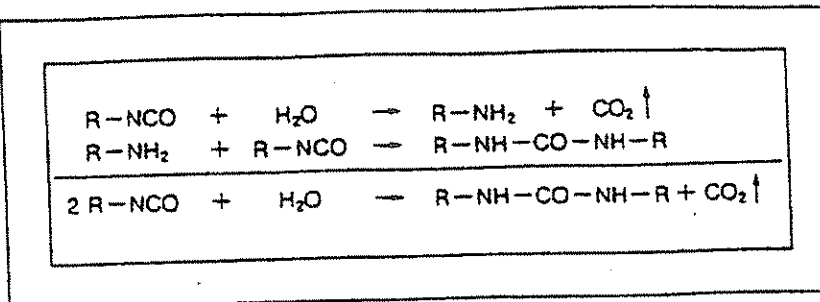


Figure 19: Polyurea Formation

drying times depend not only on the temperature but also on the amount of atmospheric moisture. With very low absolute moisture content (e.g., in winter) the drying times may be increased.

The weathering properties of one-component coatings also largely depend on the type of isocyanate used. Types based on TDI or MDI have a tendency to yellow in the light and to show a relatively rapid loss of gloss on weathering; types based on HDI are light-stable. Depending on the composition, HDI based coatings may also be equivalent in gloss retention and chalking behavior to two-component coatings that are based on Desmodur N polyisocyanates. One-component urethane coatings have very good mechanical properties. The films can range from hard to very flexible. Their surfaces are particularly mar-resistant, and their abrasion resistance is exceptionally high. The films also have good resistance to chemicals, including the stronger organic acids as well as alkalis, alcohols, solvents and water.

#### Pigmented Coatings:

Due to the sensitivity of one-component coatings to moisture, a special technique has to be followed when formulating pigmented coatings. This involves the use of pTSI and Additive OF and splitting the grind procedure into several steps. This process may be accomplished in the same amount of time as the milling of an alkyd resin and can be done with the same equipment.

The formulation is divided into four operations:

1. Weighing
2. Predispersing
3. Dispersing in the sand mill
4. Filling

As explained in Figures 20 and 21, the individual components are weighed in the

given sequence and predispersed with the dissolver. In so doing, two processes occur simultaneously:

- Homogenization of the weighed materials.
- Dehydration of the pigments, extenders and solvents by pTSI.

Carbon dioxide, released through the chemical reaction between water and pTSI, acts as a buffer gas and prevents contact with air and humidity. While the dissolver charge is warm, it can be dispersed in the sand mill.

After cooling, the catalyst, and if necessary Additive OF, can be added and the formulation adjusted to the desired application viscosity with anhydrous solvents. The material should then be packed in dry, airtight containers.

Another method of formulating pigmented coatings is to add the pigment in the form of a paste colorant. In this case, the pigment mill base can be prepared in a binder which reacts as little as possible with the NCO group. The incorporation of pTSI ensures that the pigment paste is free of water. The paste may then be mixed with the Desmodur E binder (such as Desmodur E-21).

#### Curing:

The drying rate of one-component coatings is dependent on the relative atmospheric humidity and temperature. Low temperature and low atmospheric humidity may slow down the drying considerably.

As with two-component systems, one-component coatings based on aliphatic polyisocyanates often require the incorporation of reaction accelerators. Metal compounds are especially suitable for this purpose.



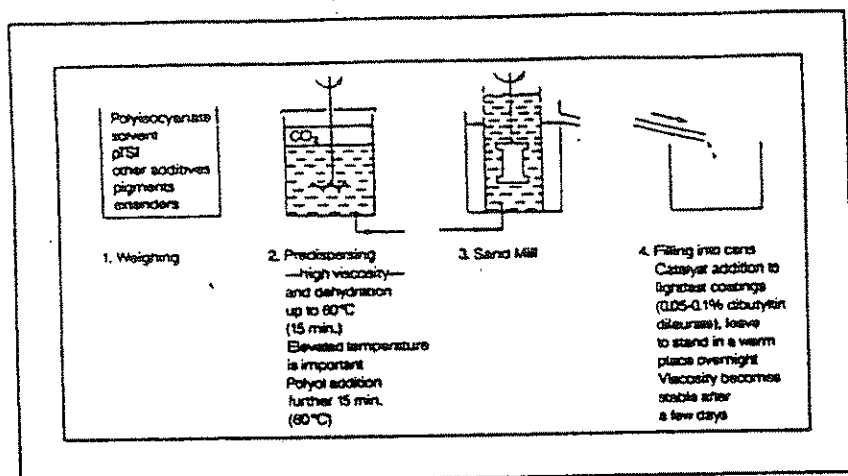


Figure 20: Formulation of pigmented one-component coatings from polyisocyanate/polyol

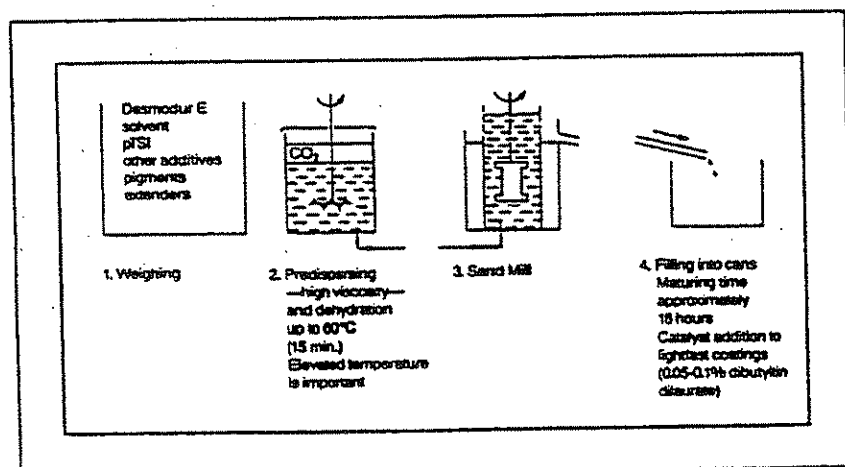


Figure 21: Formulation of pigmented one-component coatings from Desmodur E polyisocyanates

#### Application:

Moisture-curing coatings based on the Desmodur E polyisocyanates are normally applied by brushing or spraying. Dip coating and curtain coating cannot generally be used because of the extended contact between the liquid coating and atmospheric moisture.

Unpigmented one-component coatings are used principally for wood substrates (parquet, indoor application). Another area of application is the impregnation or coating of concrete which also includes decorative seamless flooring.

Pigmented one-component coatings can be used, among other things, for anti-

corrosion coatings for metals, for the surface treatment of concrete or asbestos cement and for various decorative coatings.

#### IX. Recoatability

Good intercoat adhesion is necessary for multi-coat systems. Prolonged coating intervals may impair intercoat adhesion of one- and two-component coatings. Coating intervals should not exceed 24 to 28 hours depending on the degree of through hardening.

In the case of longer coating intervals, slight intermediate sanding or appropriate priming may be required to ensure adhesion.

This does not, of course, apply to such systems designed for overcoating at a later date, such as shop-primers or those specifically formulated for use as primers or adhesion promoters.

#### X. Storage

Particular care must be given to the storage of any Mobay polyisocyanate that contains isocyanate groups. Containers of these products must be kept tightly sealed since their reaction with atmospheric moisture leads to an increase in viscosity and, eventually, gelation. Since carbon dioxide is a product of the reaction of isocyanates with water, pressure buildup and possible rupture of sealed containers of contaminated polyisocyanates can occur.

Containers used to store polyisocyanates should be inspected prior to use to be certain they are clean and dry.

Moisture should also be excluded from stored polyester, polyether, or acrylic coreactants. Most of these materials are hygroscopic and will absorb and retain atmospheric moisture. Water contamination of the polyols may lead to inferior film properties when combined with polyisocyanates.

All legal regulations concerning the storage of Mobay products must be observed.

#### XI. Health and Safety Information

Appropriate literature has been assembled which provides information pertaining to the health and safety concerns that must be observed when handling Mobay products mentioned in this publication. For materials mentioned that are not Mobay products, appropriate industrial hygiene and other safety precautions recommended by their manufacturer should be followed. Before working with any product mentioned in this publication, you must read and become familiar with available information concerning its hazards, proper use, and handling. This cannot be over-emphasized. Information is available in several forms, e.g., material safety data sheets and product labels. Consult your Mobay representative or contact the Industrial Hygiene and Regulatory Compliance Group of the Coatings Division.

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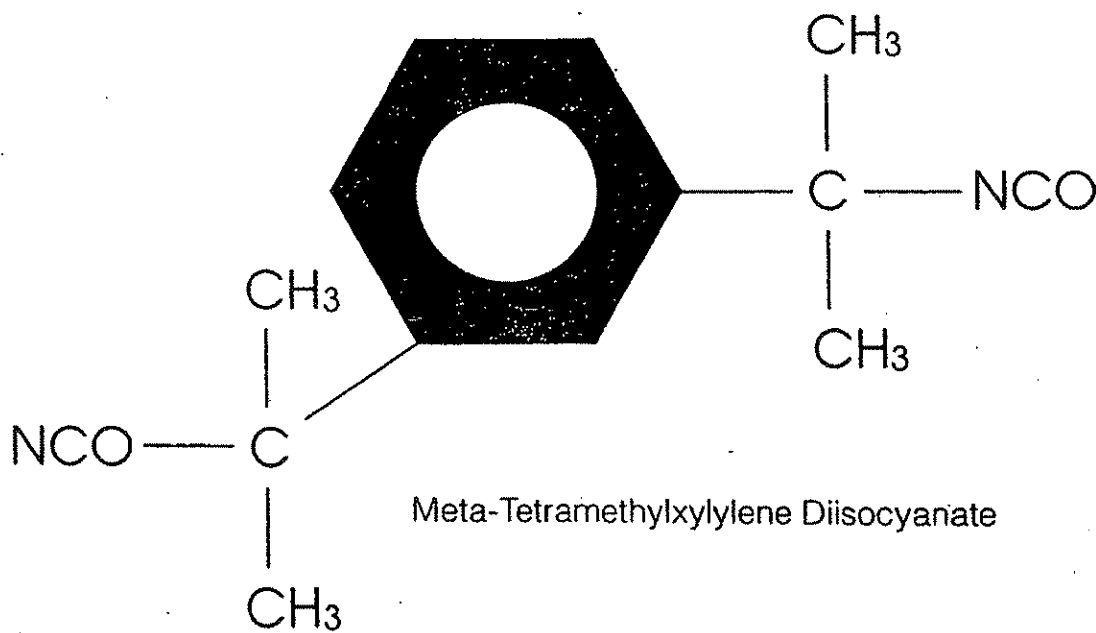
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**CYTEC**

TMXDI® (META) Aliphatic Isocyanate

**TMXDI**



Meta-Tetramethylxylylene Diisocyanate

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## I. Introduction

### OVERVIEW

TMXDI® (META) aliphatic isocyanate is a versatile aliphatic isocyanate finding broad end-use applicability. Polyurethanes based on TMXDI (META) aliphatic isocyanate are characterized by excellent weatherability, durability and hydrolytic resistance. In addition, prepolymers have proven to be significantly less viscous than those based on conventional aliphatic isocyanates and have resulted in cured systems with improved elongation. The toxicological profile of TMXDI (META) aliphatic isocyanate is also attractive. Studies from animals and humans have not detected allergic lung reactions from TMXDI (META) aliphatic isocyanate. Workplace exposure limits which make it easier to work safely with TMXDI (META) aliphatic isocyanate than with other isocyanates have been established.

### CHARACTERISTICS

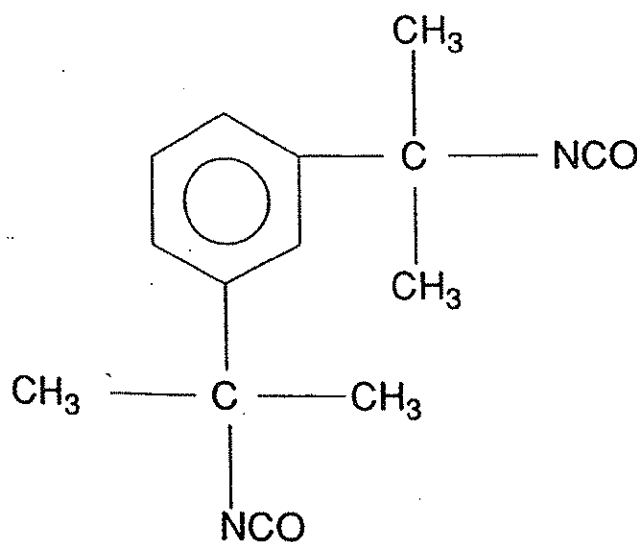
Versatile Reactivity  
High Elongation  
Low Prepolymer Viscosity  
High Filler Receptivity  
Prepolymer Thermal Stability  
Hydrolytic Stability  
Excellent Weatherability  
Favorable Toxicity

**APPLICATION AREAS**

Specialty Coatings  
 Aqueous Dispersions  
 Roof and Deck Coatings  
 Floor Coatings  
 Concrete and Wood Coatings  
 Adhesives  
 Potting Compounds  
 Sealants  
 Adhesives  
 RIM Urethanes  
 Thermoplastics  
 Lacquers

**PHYSICAL PROPERTIES**

Empirical Formula	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>
Molecular Weight	244.3
NCO Content, % by Weight	34.4 (Theoretical)
Equivalent Weight	122.1
Melting Point, °C	-10°
Boiling Point, °C	150° @ 3 mm Hg
Vapor Pressure, mm Hg at 25°C	0.003
Viscosity, cps at 0°C	25
20°C	9
80°C	—
Flash Point (Closed Cup) °C	93°
Autoignition Point, °C	450°
Specific Gravity	1.05
Solubility	Inert Organic Solvents
Total Chlorides	Typically Less Than 50 ppm
Appearance	Colorless, Clear Liquid



meta-Tetramethylxylylene Diisocyanate

## II. Chemical and Performance Characteristics

### REACTIVITY AND CATALYSIS

The reactivity of TMXDI (META) aliphatic isocyanate is in essence programmable.<sup>1</sup> For a given application the gel time, pot life, tack time and hardening time can be controlled by the choice and amount of catalyst used. Several catalyst systems have been evaluated for TMXDI (META) aliphatic isocyanate when reacting with hydroxyl compounds. In our experience dimethyltin dilaurate has been found to be a very effective catalyst. Lead octoate, dibutyltin dilaurate and tetrabutyl diacetoxystannoxane are also effective. Additionally, amines and amine salts can be utilized.

Positive synergistic effects have been observed by combining several catalysts. The advantages associated with using a combination of organic tin and lead compounds,<sup>1</sup> organic tin compounds and amine salts,<sup>2</sup> and organic tin and lead compounds with amine salts<sup>3</sup> have been demonstrated.

<sup>1</sup> U.S. Patent 4,548,919

<sup>2,3</sup> U.S. Patent 4,598,103

readily used in many applications, the most common way of introducing the isocyanate is in the form of a polyurethane prepolymer.

Both polyether and polyester prepolymers of TMXDI (META) aliphatic isocyanate are readily prepared following standard laboratory procedures. Specifically, the polyol, catalyst and solvent are stirred as TMXDI (META) aliphatic isocyanate is added slowly. The solution is heated at 85°C for 3-4 hours with the final % NCO determined by titration. For polyester-based prepolymers, adipates and caprolactones, 0.01% dibutyltin dilaurate (DBTDL) on resin solids is recommended as catalyst while 0.001% DBTDL on resin solids is recommended for polyether polyols, PTMEG and PPG.

### OPTIMIZING A FORMULATION

When TMXDI (META) aliphatic isocyanate is formulated as a direct replacement for other aliphatic isocyanates the resulting urethane is usually softer and has increased elongation. The properties of TMXDI (META) aliphatic isocyanate can be readily adjusted to meet specific application needs by the reformulating methods outlined in Table 1.

As illustrated, and expected, the property matrix is directly related to crosslinking. Increasing crosslinking increases modulus and tensile strength at the expense of elongation. For TMXDI (META) aliphatic isocyanate, increased crosslinking can be achieved through several mechanisms. These mechanisms include using a multifunctional polyol in the prepolymer, using a lower molecular weight polyol in the prepolymer, and using a multifunctional chain extender or curative.

### PREPARING A PREPOLYMER

Polyurethanes comprised of aliphatic isocyanates may be applied through one of several means including spray, solid cast or solution cast systems. The choice of method is dependent upon the materials used and the restrictions and requirements of the application. While the isocyanate monomer can be

**Table 1**

**Reformulation as a Tool to Tailor TMXDI (META) Aliphatic Isocyanate Properties**

Reformulate Via	Property +/-		
	Hardness	Tensile	Elongation
Add Difunctional Polymer	-	-	+
Add Multifunctional Polyol			
(Greater than 2)	+	+	
Cure/Extend with Trifunctional	+	+	
Change High MW Polyol to Low MW	+	+	

## ELONGATION

The elongation observed for several polyurethanes is illustrated in Table 2. Elastomers based on TMXDI (META) aliphatic isocyanate demonstrate higher elongation as compared to identical systems made from hydrogenated diphenyl methane diisocyanate (H<sub>12</sub>MDI) and isophorone diisocyanate (IPDI). The systems described are formulated using equal isocyanate equivalents.

Elongations as large as twice those of competitive systems have been observed in several systems when formulating by isocyanate equivalent weight. The higher elongation is attributed to the urethane hard segment. For the polyurethanes based on TMXDI (META) aliphatic isocyanate the hard segment is not as strongly hydrogen-bonded as those of competitive systems, hence, the elongation is greater. The reduced strength of the hydrogen bond manifests itself in a lower modulus and hardness when compared to H<sub>12</sub>MDI and IPDI. Higher elongations are still observed if the system is formulated to achieve the same hardness as competitive systems.

## VISCOSITY

In addition to higher elongation, considerably lower viscosities are observed for prepolymers based on TMXDI (META) aliphatic isocyanate in comparison to the competitive systems. Viscosities recorded at 70°C for several systems are found in Table 3.

The lower viscosity of prepolymers based on TMXDI (META) aliphatic isocyanate allows for a higher solids level before significant viscosity increase impairs

**Table 2**

### Elongation of Polyurethanes Based on TMXDI (META) Aliphatic Isocyanate Versus IPDI and H<sub>12</sub>MDI Polyurethanes

System	% Elongation		
	TMXDI (META) Aliphatic Isocyanate	IPDI	H <sub>12</sub> MDI
<b>Castable Elastomer</b>			
Tone 240*	446	400	362
PEA 2100	595	520	456
PTMEG	508	440	440
<b>Two Component</b>			
PPG	359	320	174
Hexanediol Adipate	358	218	244
Tone 240/305*	204	112	102
<b>One Component</b>			
Tone 230/305*	302	227	240

\*Products of Union Carbide Corporation

**Table 3**

### TMXDI (META) Aliphatic Diisocyanate Prepolymer Viscosity Characteristics

Polyol	Prepolymer % Solids	Viscosity (Brookfield, CPS, 70°C)		
		TMXDI (META) Aliphatic Isocyanate	H <sub>12</sub> MDI	IPDI
Tone 230/305*	65 (toluene)	220	970	340
Tone 240*	100	1255	1965	1540
HD-AA	100	2300	100,000	100,000
HD-AA	85 (NMP)	400	1300	780
BD-AA	85 (NMP)	650	4050	1500
HD-AA-IPA	100	2700	200,000	4500

\*Products of Union Carbide Corporation

processing. In addition, the lower viscosity leads to a more easily processed system and the preparation of low volatile organic compound (VOC) systems.



## STABILITY

Polyurethane prepolymers prepared with TMXDI (META) aliphatic isocyanate have excellent thermal stability.<sup>4</sup> No significant change in NCO content is observed following storage at an elevated temperature of 100°C over a 14-day period. NCO levels are determined by titration.

Another characteristic that demonstrates the versatility of urethanes based on TMXDI (META) aliphatic isocyanate is their resistance to hydrolysis conditions as measured by ASTM Test Method D-3137 and outlined in *Table 4*. The very favorable combination of high elongation and tensile strength remains even after 4 days in a 100% relative humidity environment at 85°C. Appreciable levels of tensile strength and elongation are still observed if the test period is expanded to four weeks.

<sup>4</sup> *Elastomerics*, 1985, June; *Polyurethane Manufacturers Association, Technical Papers*, 1987, April

**Table 4**

### Hydrolytic Stability of PTMEG Castable Elastomers (ASTM D3137) Based on TMXDI (META) Aliphatic Isocyanate

Properties	Original	After Hydrolytic Conditions*
Hardness, Shore A	90	89 (99%)
Shore D	35	32 (91%)
100% Modulus, psi	887	839 (95%)
Tensile Strength, psi	6203	5512 (89%)
Elongation, %	508	575 (113%)

\* 4 days at 85°C, 100% relative humidity

**WEATHERABILITY**

The weathering of polyurethanes based on TMXDI (META) aliphatic isocyanate parallels that of other aliphatic isocyanates in that surface quality and gloss retention are excellent. Gloss retention observed for a urethane roof topcoat with TMXDI (META) aliphatic isocyanate and for a comparable system made with H<sub>12</sub>MDI. The two systems were exposed to artificial weathering conditions, specifically Xenon arc. CUV values parallel the Xenon arc data in the table. As demonstrated, the weatherability of

the system based on TMXDI (META) aliphatic isocyanate exceeds that observed for the H<sub>12</sub>MDI system.

Although the molecule of TMXDI (META) aliphatic isocyanate is built around an aromatic ring, the isocyanate functionalities are not conjugated and are aliphatic. Thus, the quinoid structures which give rise to the poor weatherability of true aromatics, such as toluene diisocyanate (TDI), are not possible. In addition, the presence of methyl groups in the place of benzylic hydrogens further enhances the UV stability.

**Table 5**

**Weathering of TMXDI (META) Aliphatic Isocyanate in a Roof Coating Formulation Versus H<sub>12</sub>MDI Based Systems**

	Gloss Retention, %*	
	TMXDI (META) Aliphatic Isocyanate	H <sub>12</sub> MDI
Xenon-1,000 Hours	100	61
Xenon-2,000 Hours	100	24

\* CUV systems was approximately 35

### III. Applications

#### AQUEOUS POLYURETHANE DISPERSIONS

Polyurethane dispersions bring the performance advantages of solvent-borne urethanes to aqueous systems. These advantages include toughness, abrasion resistance, hydrolytic stability, hardness, elasticity and light stability.

The use of TMXDI (META) aliphatic isocyanate in aqueous polyurethane dispersions gives coatings and dispersion systems that have several advantages over those that are currently marketed with competitive aliphatic isocyanates. Included among these advantages are coatings with high tensile strength and high elongation; prepolymers with lower viscosity; lower cosolvent levels, which leads to significantly lower VOC levels; and higher solids capability at lower viscosities. Dispersions based on TMXDI (META) aliphatic isocyanate that are solvent-free and have a low VOC content are readily obtainable. Generally, film properties of dispersions based on TMXDI (META) aliphatic isocyanate are comparable to those made from H<sub>12</sub>MDI and IPDI. The hardness, flexibility, chemical, solvent and stain resistance are equivalent. TMXDI (META) aliphatic isocyanate based dispersions when formulated to have equal tensile strength will have higher elongations than those produced from H<sub>12</sub>MDI and IPDI.

#### ROOFING, FLOORING, UV- CURING SYSTEMS

Systems based on TMXDI (META) aliphatic isocyanate make excellent topcoats for roofing, decking and flooring. Moisture cure and two-component systems are readily prepared for roofs and decks while UV-cure systems are particularly well suited for vinyl flooring.

Two-component systems can be set-to-touch in two hours and hard-dry in four hours. These systems are characterized by high tensile strength and high elongation. The characteristic high elongation of polyurethane elastomers cured with TMXDI (META) aliphatic isocyanate is of particular benefit in roof coatings.

Both polyether-polyurethane and polyester-polyurethane UV-curable compositions are feasible with TMXDI (META) aliphatic isocyanate. A UV-curable system modified with TMXDI (META) aliphatic isocyanate results in excellent physical properties and adhesion to the substrate. These systems are also characterized by lower viscosity and a better combination of stain and abrasion resistance when compared to competitive systems.

#### SOLID CASTABLE ELASTOMERS

Solid castable elastomer systems based on TMXDI (META) aliphatic isocyanate are readily prepared and polyester or polyether polyurethanes are viable depending on application requirements. When evaluating versus other aliphatic isocyanates, castable elastomers based on TMXDI (META) aliphatic isocyanate result in comparable or superior properties. When TMXDI (META) aliphatic isocyanate is formulated to have tensile strength and hardness equivalent to H<sub>12</sub>MDI and IPDI based elastomers, the elongation of the system based on TMXDI (META) aliphatic isocyanate is higher than that of the alternate systems. When subjected to thermal resistance, hydrolytic resistance, humidity resistance, and water immersion tests, the castable elastomers based on TMXDI (META) aliphatic isocyanate retained tensile strength, elongation and hardness as well as their H<sub>12</sub>MDI and IPDI based counterparts.

## ADHESIVES

TMXDI (META) aliphatic isocyanate is also suitable for one-package, heat-curable urethane adhesives. This application takes advantage of the rather slow kinetics observed in the absence of an active catalyst. Certain latent catalyst systems become highly active when heated and contribute to the versatility of adhesive systems based on TMXDI (META) aliphatic isocyanate. Excellent lap shear strengths are realized in properly formulated systems.

TMXDI isocyanate is sanctioned by the U.S. FDA for use in food packaging adhesives under 21 CFR 175.105. The use of TMXDI isocyanate in the manufacture of polyurethane dispersions utilizing DMPA (dimethylolpropionic acid) and TEA (triethylamine), as applicable under 21 CFR 175.105, continues to grow due to TMXDI dispersion manufacturing ease, extremely low VOC potential (0.3 lbs/gal), and high adhesive performance properties. In addition to TEA, we have expanded the FDA sanction of TMXDI isocyanate under 21 CFR 175.105 to include its reaction with four alternative amines.

## REACTION INJECTION MOLDING

In the RIM process, low viscosity liquids are mixed and pumped into a mold under pressure, typically 50 to 100 psi. When formulated for fast cure, large, complicated urethane parts can be made with cycle times of two minutes or less.

Both TDI and MDI-based urethanes discolor and lose surface gloss and strength in the presence of UV light. UV stabilizers can be added to protect the urethane from photo-degradation, but they provide limited improvements in weathering resistance. For acceptable performance an aliphatic topcoat must be applied through either post-painting or in-mold coating. Both UV stabilizers and an aliphatic topcoat add to the system costs.

Using an aliphatic isocyanate in the structural urethane significantly improves the weathering resistance of RIM parts and eliminates the need for a coating. Thus, light-stable urethanes made with aliphatic isocyanates are useful in applications where a protective coating is difficult to apply or undesirable.

Molding of modular window gaskets is an application which combines the productivity of RIM with the versatility of polyurethanes. Light-stable urethanes based on TMXDI (META) aliphatic isocyanate exhibit the physical properties, aging, weathering resistance and adhesion to glass needed for modular window gaskets. Property retention after 14 days of heat and humid air aging is excellent as greater than 90% of the original properties (tensile, elongation, modulus) are retained. Weathering of the system is superior. There is no loss of gloss or surface cracking following 1500 hours of GM-WOM exposure and property retention after weathering is also excellent. One aspect of this application of particular interest is the adhesion of the polyurethane based on TMXDI (META) aliphatic isocyanate to glass. In 180° peel tests, values of over 40 psi are consistently obtained. This well exceeds the minimum adhesion requirements for modular window gaskets.

## TOXICOLOGY

TMXDI (META) aliphatic isocyanate has demonstrated favorable toxicological properties. Unlike most aliphatic isocyanates TMXDI isocyanate is not a pulmonary sensitizer. Based on health effects studies in animals and humans, Cytec has established a PEL (permissible exposure level) and STEL (short-term exposure level) for TMXDI (META) aliphatic isocyanate. The PEL is 50 ppb as an 8-hour time-weighted average and the STEL is 100 ppb as a 15-minute time-weighted average. The basis for the PEL is lung injury with repeated inhalation exposure. In contrast, the 8-hour time-weighted average threshold limit value (TLV) for other isocyanates is 5 ppb.

Hence, working safely with TMXDI (META) aliphatic isocyanate is easier than with other aliphatic isocyanates. TMXDI (META) aliphatic isocyanate should be handled with care, as should all isocyanates, due to known toxic hazards. Direct skin contact can cause allergic skin reactions. Overexposure to vapor can cause eye irritation and repeated inhalation may cause injury due to irritation of the lung and respiratory tract. Cytec's toxicological documentation of TMXDI (META) aliphatic isocyanate is extensive. Detailed information is available upon request.

## HEALTH AND SAFETY

TMXDI (META) aliphatic isocyanate may be harmful with inhalation overexposure and vapor can cause eye and respiratory tract irritation. Skin exposure to the liquid can cause dermal sensitization. It should be used in well-ventilated enclosures with use of impervious gloves, chemical splashproof goggles and respiratory protection (where necessary) to prevent skin, eye and/or vapor exposure. Based on evaluations of the effects on respiratory function, Cytec Industries has established a permissible exposure level of 50 ppb as an 8-hour time-weighted average. The short-term exposure level is 100 ppb as a 15-minute time-weighted average.

For further information on health hazards and recommended safe handling requirements, read the Cytec Material Safety Data Sheet 1344. Detailed toxicological information is available upon request.

## STORAGE

TMXDI (META) aliphatic isocyanate is sensitive to moisture and should be kept in tightly closed original containers to prevent contamination with moisture and air. If partially filled containers are stored, it is advisable to blanket the liquid with dry air or nitrogen before sealing. Ambient storage temperatures should not exceed 80°F.

## TECHNICAL INFORMATION

For additional technical assistance call the Urethane Chemicals Technical Service Group: 1-203-321-2374.

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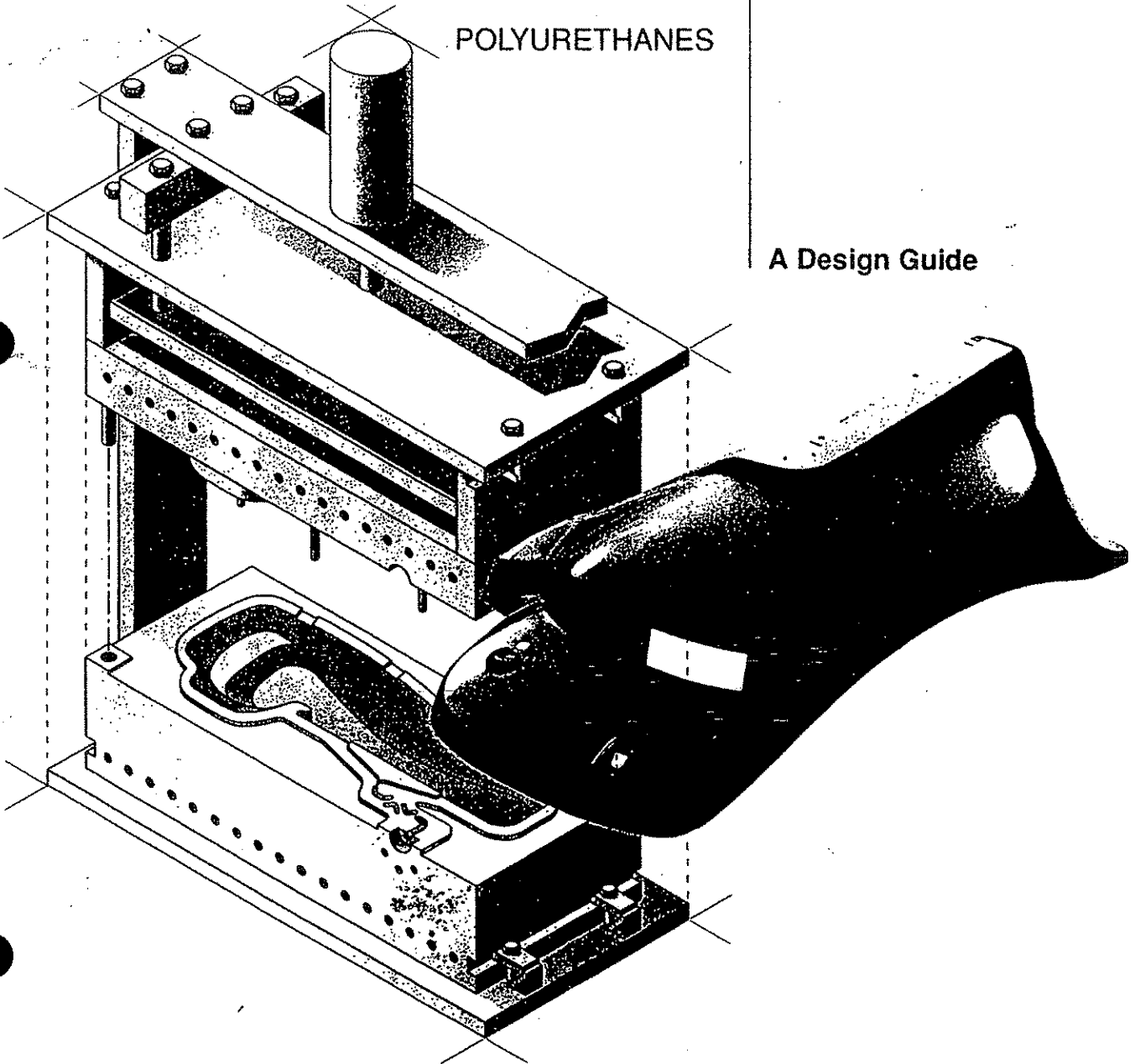


Engineering Polymers

## ***RIM Part and Mold Design***

POLYURETHANES

A Design Guide



CW 0308681

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Introduction  
**PART DESIGN**

Today, various Reaction Injection Molding (RIM) polyurethane systems are replacing many traditional materials because of their inherent advantages, including:

- Large-part molding;
- Wall-thickness variations;
- Excellent encapsulation capabilities;
- Excellent surface reproducibility and in-mold paint finishing;
- Good dimensional stability;
- Good chemical resistance;
- Good weatherability.

Generally, RIM processing uses less-expensive molds, less energy, and lower-tonnage presses than thermoplastic processing. These characteristics add up to superior design, economic, and processing flexibility.

The extensive number of RIM polyurethane systems with their various physical and mechanical properties can make selecting the right system difficult. The purpose of this manual is to help you — the design engineer, product designer, and others who work with RIM polyurethane materials — make practical design decisions.

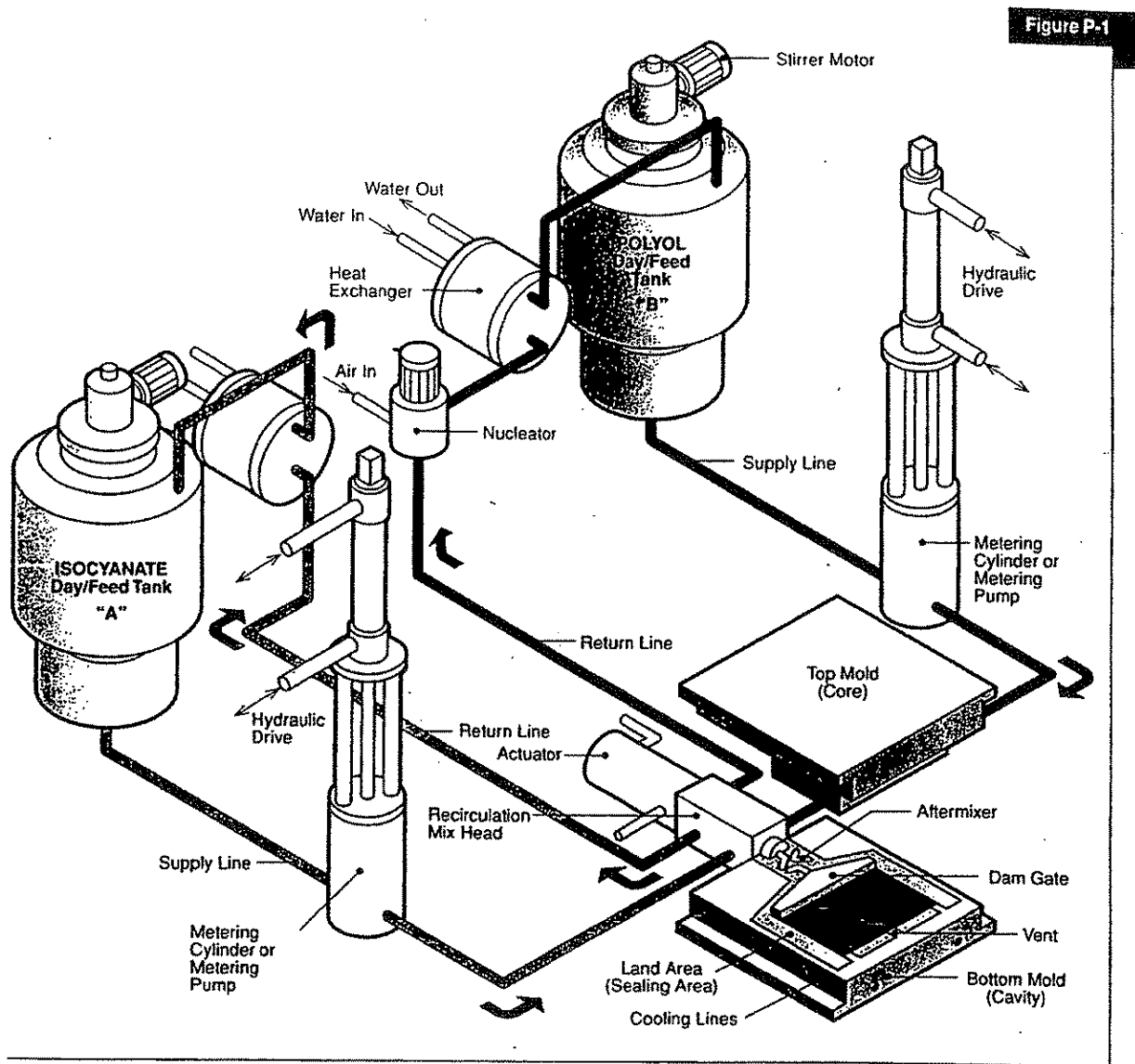
This manual is divided into two sections: part design and mold design. The section on part design begins with a brief discussion of the RIM polyurethane process and design considerations common to all RIM polyurethane systems. Unique properties and design guidelines for various polyurethane systems are discussed next, followed by design considerations for assembly and postmolding operations. The second section of this book contains information on mold, gate, and runner design.

Many rules of thumb appear in the text. Naturally, there may be some exceptions to these rules of thumb or times when one conflicts with another. If this happens, talk with your mold maker/designer and Bayer Corporation personnel for appropriate action. While this manual provides a good overview of the topics you should address when designing for polyurethane parts, you should also have a good understanding of polyurethane systems before making

final decisions. For a quick reference, see the part-design matrix on the inside back cover for key information.

Specific system data and typical property information have not been included in this manual except as examples for general information. All values that appear in this manual are approximate and are not part of the product specifications. Do not use this data for product specification. For more specific information on a particular system, please read the appropriate Bayer Product Information Bulletin (PIB). Published data should be used to screen potential material candidates. Your understanding of materials and processing and your part's requirements determines the suitability of a material for your product or application. Ultimately, material selection must be based upon your prototype testing under actual, end-use conditions.

Bayer offers a full range of RIM polyurethane systems, including foamed, solid, and structural composite materials. As a service to our customers, we also have technical personnel ready to help you with part design and production. A list of these services appears in the back of this booklet. Please feel free to contact us with specific questions at 412 777-2000.



Reaction Injection Molding (RIM) process.

## Introduction

**PART DESIGN** *continued***THE RIM PROCESS**

In contrast to thermoplastics where a molten plastic is compacted in a mold and then solidifies upon cooling, RIM systems are composed of two liquid components that chemically react to form plastic material in a mold. The liquids, isocyanate and polyol, are commonly referred to as the "A side" and "B side" components, respectively, in the United States. In Europe, these demarcations are reversed. A matched set of "A" and "B" components is referred to as a "RIM system."

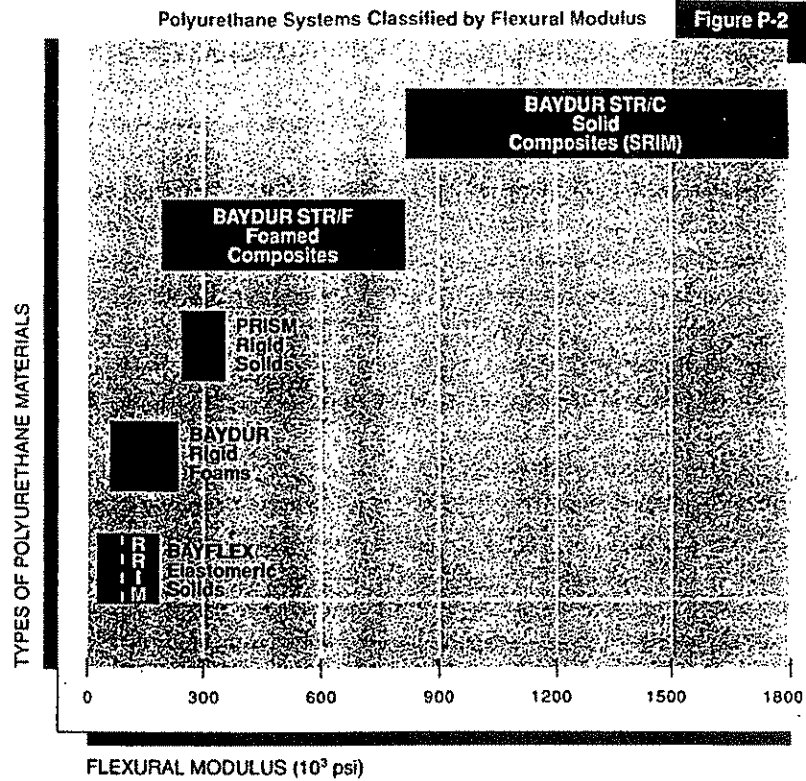
Generally, the "B" component contains additives such as stabilizers, flow modifiers, catalysts, combustion modifiers, blowing agents, filler, pigments, and release agents to modify physical characteristics in the final part. When the "A" and "B" components combine, the isocyanate reacts with the hydroxyl in the polyol to form a thermosetting polyurethane polymer. This reaction is exothermic: when the "A" and "B" components combine, heat is released. To prevent scorching and/or other part defects, cooling lines on the mold help dissipate this heat.

In figure P-1, the pressurized day tanks typically hold from 30 to 250 gallons of isocyanate or polyol. Recirculation pumps and agitators maintain a homogeneous blend of the individual components. The heat exchangers maintain components' temperature. Either high-pressure, metering pumps or hydraulically driven chemical cylinders — commonly referred to as "lances" — meter isocyanate and polyol into the mixing head. Flow rates and pressures are precisely controlled to ensure high-quality parts.

The mix head contains injector nozzles which impinge the isocyanate and polyol at ultra-high velocity to provide excellent mixing. Additional mixing is accomplished using an aftermixer, typically constructed inside the mold.

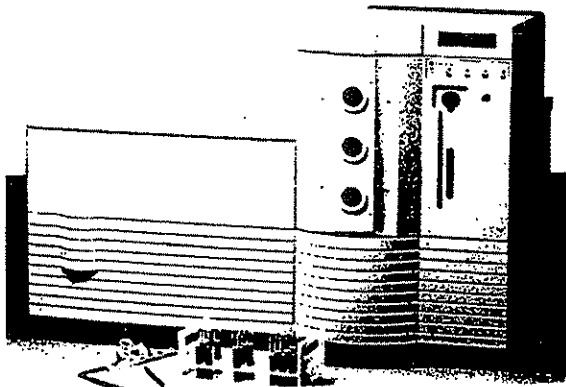
## MATERIAL DESCRIPTIONS

The degree of rigidity usually defines a polyurethane system, placing it in one of two categories: rigid or elastomeric. A rigid polyurethane material generally has a higher flexural modulus and degree of hardness. This class of materials normally offers good thermal resistance, electrical properties, chemical resistance, and acoustical insulation. An elastomeric polyurethane system is often found in applications requiring superior impact strength. Elastomeric polyurethane systems exhibit good toughness and dimensional stability throughout a wide temperature range and have excellent corrosion, abrasion, wear, and cut resistance.



Physical properties for these two categories are not absolute and the flexural moduli ranges of these materials overlap (see figure P-2). Within these two classifications, there are three types of polyurethane systems (see figure P-3):

- Foamed polyurethane systems use a blowing agent to make parts with a higher-density skin and a lower-density, microcellular core in a sandwich-like composition. Baydur structural foam and other rigid systems have hard, solid skins and are found in business machines, electronic and medical housings, automobile spoilers, skis, and other load-bearing applications. All foamed RIM materials are microcellular systems, having cells as small as 0.001 inch.



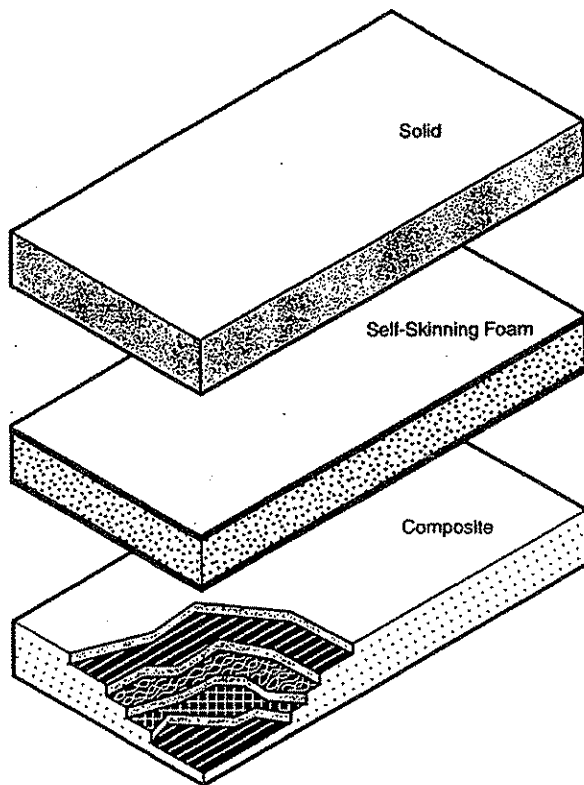
- Solid polyurethane systems do not use blowing agents, resulting in a *homogeneous*, rigid or elastomeric plastic. Bayflex solid elastomeric materials are used in many applications, including the automotive, specialty transportation, construction, agriculture, and recreational industries. Common parts include fenders, fascias, trims, and vertical panels. Glass or mineral fillers can be added to solid elastomers for improved stiff-

ness. This is commonly referred to as Reinforced RIM or RRIM.

PRISM solid polyurethane systems have many properties similar to those of engineering thermoplastics. They can be used to mold many thicker or thin-walled parts and may be more economical than thermoplastics.

- Structural composite polyurethane systems are solid or foamed materials, molded in combination with long-fiber reinforcements, such as glass mat, to improve the system's mechanical characteristics. Sometimes referred to as "SRIM," for Structural RIM, these systems have extremely high stiffness and high impact strength because of the mat. Typical applications include door panels, shelves, automotive horizontal/load-bearing panels, and recreational-equipment parts.

Figure P-3



Types of polyurethane materials.





Backhoe fender  
molded from Bayflex  
solid elastomer.

## Chapter 1

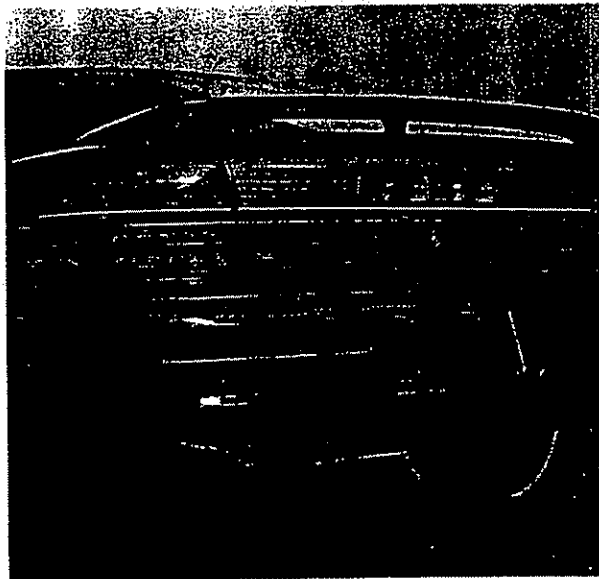
**MATERIAL SELECTION CRITERIA**

*When designing parts made of RIM polyurethane systems, make sure that your part or assembly meets all performance parameters and can be molded successfully and cost effectively. Before selecting a polyurethane system for part production, you must address three areas: aesthetic considerations, the part's functional needs, and your economic concerns. Involving the material supplier, mold maker, and molder/processor throughout a project will make the development process from concept to finished part much easier. Look in the back of this manual for a Quick Design Reference Guide for RIM Materials. See Bayer's Engineering Polymers: Property Guide for material property information.*

**AESTHETIC CONSIDERATIONS**

When establishing aesthetic requirements for your part, remember the old adage, "form follows function." If you are designing a car fascia or fender, your part will need a "class A" finish, because most automotive applications are aesthetically sensitive. On the other hand, if you are designing an unexposed structural member, aesthetics may not be as important as load-bearing characteristics. While it is important to make your part look good, specifying unusual finishes or paints can increase your post-molding costs. Some aesthetic guidelines to consider when designing parts include:

- Determine if your part will need a smooth, mirror-like, "class A" finish, a textured finish, or other type of finish because some polyurethane materials may be more suitable for your part (see photo).
- Decide if your part will need color. Polyurethane parts can be painted, pigmented, and/or in-mold coated.
- Determine if pigmentation without painting is acceptable. Darker colors — blacks, grays, or browns — may not need painting because color shifts caused by ultraviolet light will be less noticeable.



- Consider applying a good polyurethane paint or clear coat to prevent chalking or color shifts caused by UV exposure. Polyurethane coatings inherently have excellent adhesion.

### **FUNCTIONAL CONSIDERATIONS**

When defining functional requirements, consider all the environments to which your part will be exposed, as well as its end-use conditions. Ambient temperature, humidity, and UV radiation are of particular importance. Consider the following guidelines when addressing functional requirements:

- Determine if your part needs high impact resistance and/or high stiffness.
- Define the part's loading conditions, fastening or attaching parameters, and other physical requirements. The physical properties of the RIM material must withstand the structural conditions to which your part will be subjected.
- Determine the chemicals to which your part may be exposed during processing and assembling, as well as in end use. These include, but are not limited to solvents, degreasers, cleaning agents, and household products. Ensure that these chemicals are compatible with your material selection.

- Determine if stiffening inserts should be encapsulated in the part.

- Consider elastomeric RIM polyurethane systems, if your part needs good impact characteristics.

- Consider rigid polyurethane systems for parts that need high stiffness.

- Use a structural composite polyurethane system if your part needs high stiffness and high impact strength.

- Use self-skinning, rigid, foamed systems when you need to reduce density and part weight.

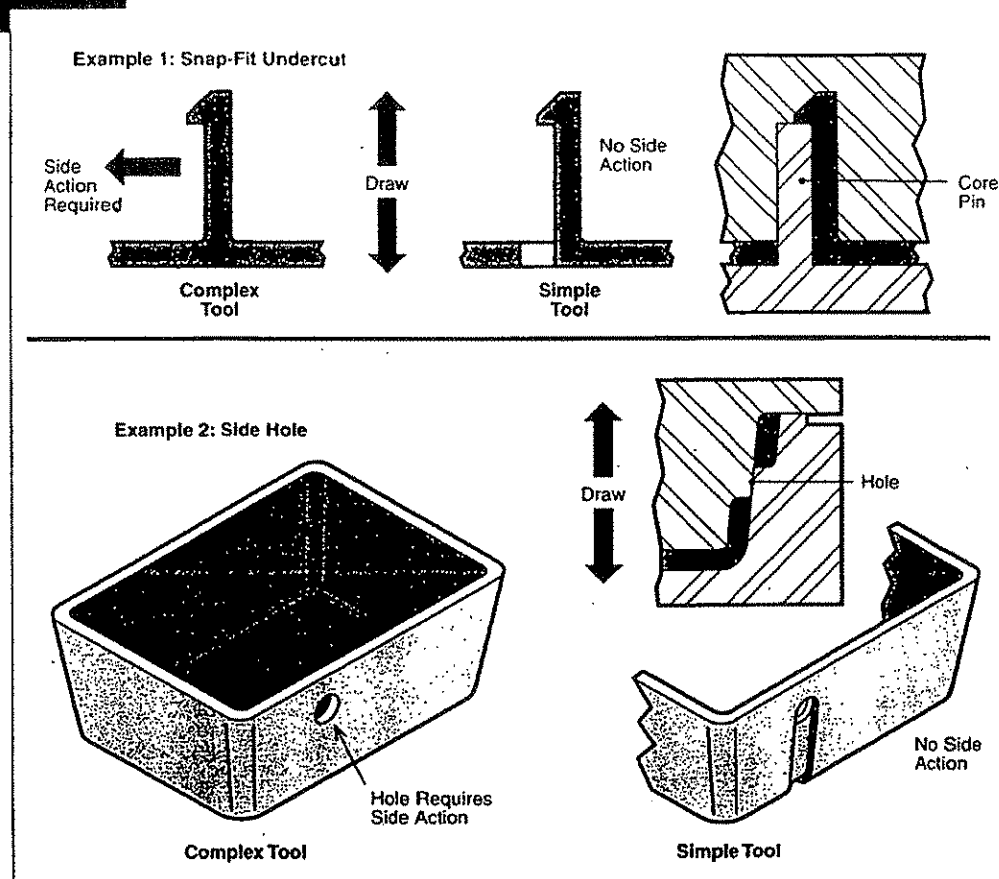
- Use Bayer's *Engineering Polymers: Material Selection* and consult with your Bayer representative for more information on material selection.

### **ECONOMIC CONSIDERATIONS**

The final cost of a part involves more than the per-pound cost of the material. Different materials — steel and plastic, for instance — have different costs associated with processing, finishing, productivity, and quality control — all of which can alter the cost dramatically. RIM polyurethane systems, for instance, offer quick cycle times for large parts made of elastomers and, in many cases, can use less-expensive equipment than thermoplastics. Additionally, parts made of polyurethane may weigh less than comparable parts made of other materials.

Because the part's shape, not its weight, is fixed in the design, you should also compare the cost per volume ( $\$/\text{in}^3$ ) instead of cost per pound. A ton of low-



**Figure 1-1**

Simple/complex part design for undercuts.

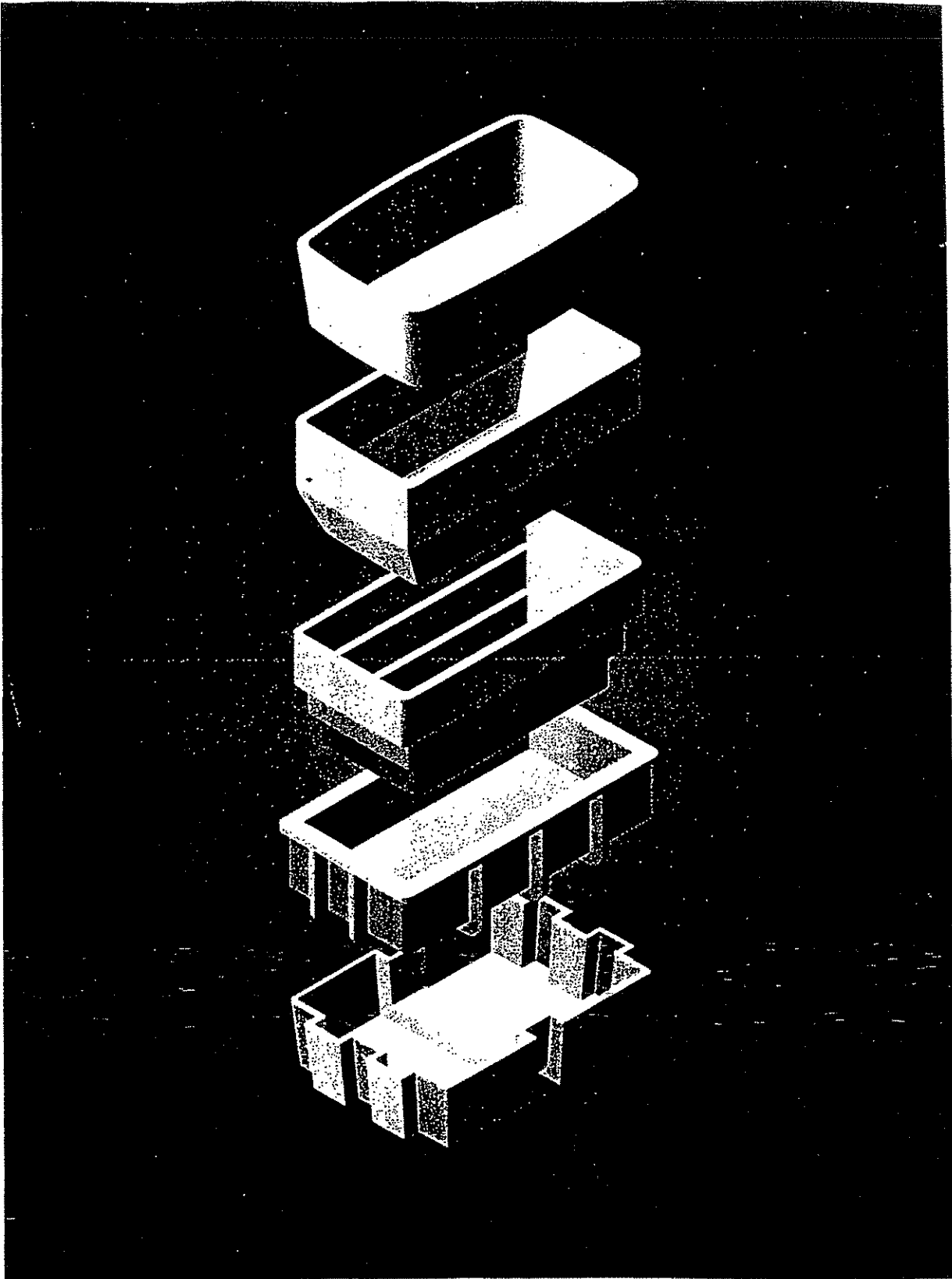
density material will produce more parts than a ton of high-density material.

Part geometry also plays an important role. When comparing polyurethane systems for a load-bearing application, optimize part geometry for each material's characteristics. For example, you may be able to design a part with thinner walls and fewer ribs to achieve the required stiffness by using a

higher-density system. Consider these guidelines when determining costs:

- Identify your cost target.
- Know the current cost of manufacturing and assembly, particularly when replacing a part made using a different process.
- Optimize wall thickness to reduce part weight and mold-cycle time.

- Core thick sections where possible. Use other reinforcing techniques such as ribbing, corrugating, and encapsulating structural inserts to improve the part's stiffness.
- Simplify part design. Complex parts with multiple side pulls will increase mold costs significantly (see figure 1-1).
- Consider the added costs for finishing, painting, or coating.



## Chapter 2

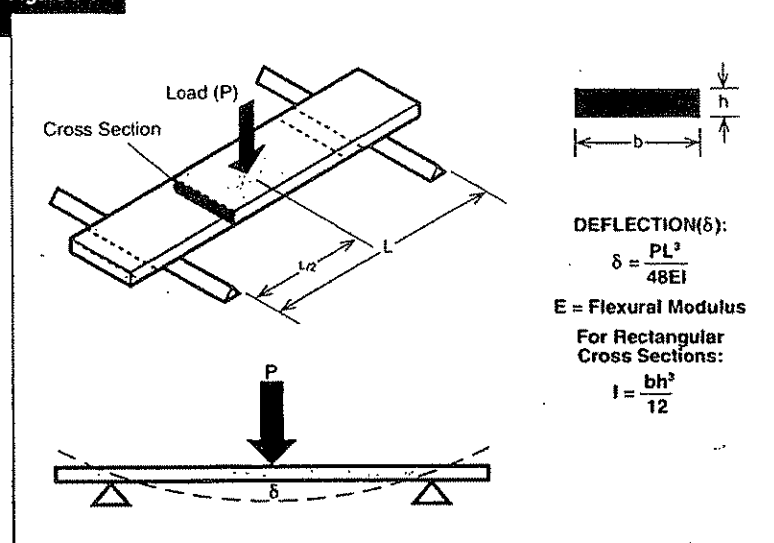
## GENERAL PART DESIGN

Other design parameters beyond material-specific guidelines must also be considered when designing parts, including:

- Wall thickness
- Warping
- Ribs and ribbing direction
- Slots
- Vents
- Grooves
- Inserts

These design parameters are discussed in this section.

Figure 2-1



Three-point loading test.

### PART STIFFNESS

When designing for part stiffness, you may have to balance a part's wall thickness and the material's flexural modulus or, in foamed systems, material density. To improve stiffness while minimizing wall thickness, consider using a higher-modulus system, improving part geometry, or adding reinforcements and encapsulations.

The flexural test, a simply supported, three-point loading test, determines the material's flexural-modulus value, the basic physical property used to determine stiffness in typical bending applications (see figure 2-1). The flexural modulus is defined as the initial slope of the stress-strain curve generated in

this test. Greater flexural modulus values indicate higher inherent stiffness. A part subjected to bending has a stiffness indicator defined as the flexural modulus multiplied by the moment of inertia, a geometric property. This indicator gives a comparative value to use when optimizing different materials and part geometries.

### WALL THICKNESS

Parts made from polyurethane systems can be designed with varying wall thicknesses more effectively than traditional thermoplastics. Thicker walls have higher stiffness.